Space Environmental Exposure of IITRI White Thermal Control Paints
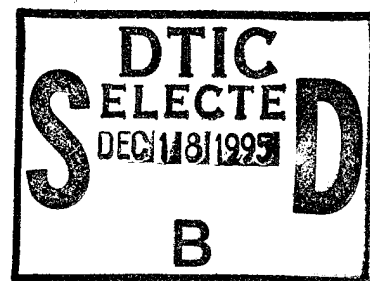
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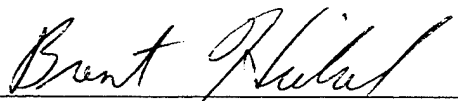2430 E. El Segundo Boulevard
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13. ABSTRACT (*Maximum 200 words*)

Extensive space simulation testing of the IITRI (Illinois Institute of Technology Research Institute) paints Z-93, S13GLO-1, and YB-71, and their reformulated replacements using a new source of potassium silicate binder material (Kasil 2130) has been performed at The Aerospace Corporation using UV and electron radiation in vacuum. Measurements of the pretest and post-test solar absorptances indicated differences in performance for these materials. For Z-93 and Z-93P, the tests have indicated that the two formulations behave nearly identically, and replacement of Z-93 with Z-93P is recommended. S13GLO-1 and its counterpart, S13GPLO-1, performed similarly, but one batch of the new S13GPLO-1 gave anomalous degradation and therefore would warrant further investigation. YB-71P has demonstrated a marked tendency toward radiation damage and is not an appropriate replacement for YB-71. The degradation observed in this new material is attributed to a reaction caused by an unidentified component of the binder producing reduction of titanium in the pigment. Additional research at IITRI will be required to address this problem.

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Preface

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EXECUTIVE SUMMARY

The white thermal paint space radiation simulation testing program was developed to test the radiative properties of three reformulated thermal control paints used on SMC satellite systems. The reformulation of the paints—Z-93, YB-71, and flexible S13GLO-1—was necessitated when the vendor of a critical paint ingredient ceased production. The results of this testing indicate that only one of the three reformulated thermal control coatings, Z-93P, is qualified for use on space systems. Further tests are needed to requalify S13GPLO-1, while the replacement for the third paint, YB-71P, cannot be requalified.

White thermal control paints are a cost-effective solution to controlling the temperatures of spacecraft systems. The three primary paints mentioned above are used on SMC and other satellite systems. All three use potassium silicate as a binder material. Formerly, the potassium silicate was supplied by Sylvania, but financial considerations caused them to discontinue production of this material. The Air Force, through the SMC Office of the Chief Engineer (SMC/EN), contracted the Illinois Institute of Technology Research Institute (IITRI) to reformulate the three thermal control paints using a Philadelphia Quartz Company substitute binder material. The contract resulted in a successful reformulation program. However, the contract did not provide for the testing of the new paints in a space environment.

White paints are used on spacecraft to control temperatures of subsystems. To perform this function, the paint must maintain its optical properties over the lifetime of the mission in space. While normally a replacement ingredient in a material formulation would be trivial, the sensitive nature of white thermal control paints to radiation damage, impurity levels, manufacturing, and process conditions dictated that a thorough investigation of the properties of the new reformulated paints be performed. To complete the process of paint reformulation and requalification, SMC/EN embarked on this program to requalify the new thermal paint formulations for use on space systems. The scope of the work at IITRI involved reformulation of the three white coatings and included extensive testing of coatings' physical and optical properties. However, no funding was included to perform space radiation simulation testing, nor was there the capability at IITRI to perform such work. This space simulation testing was performed primarily by The Aerospace Corporation, with some contributions from Wright Laboratories, NASA, and industry. This report describes the test program and data obtained from extensive space simulation testing of the reformulated paints. In retrospect, this was a necessary effort since testing indicated that a simple one-for-one replacement of this ingredient did not produce satisfactory test results for all three paints.

The results of the testing indicate that the replacement for Z-93, designated Z-93P, performed well and is recommended for immediate use on SMC space systems. Unfortunately, the replacements for S13GLO-1 and YB-71, designated S13GPLO-1 and YB-71P did not perform well. Testing indicates that, in general, S13GPLO-1 performed similarly to S13GLO-1. However, batch-to-batch variations in the paint indicate a need for further testing prior to the qualification of this paint for spaceflight. The testing of YB-71P was extremely disappointing. The paint demonstrated a marked tendency towards radiation damage. This is attributed to a reaction caused by an unidentified component of the binder producing reduction of titanium in the pigment that causes graying of the paint. Because of

this problem, YB-71P is not an appropriate replacement for YB-71, and should not be used on SMC space systems.

It is clear from the results shown in this report that, had this program not been completed, satellites using S13GPLO-1 or YB-71P may have experienced a substantial decrease in mission life due to the anomalous heating of satellite subsystems. This program has identified critical deficiencies in two reformulated white thermal control paints that will require further testing or outright replacement. Without follow-on work, we envision a serious impact to cost and schedule of those programs planning to use reformulated, but as yet unqualified, white thermal control paints.

1. Introduction

In 1989, Illinois Institute of Technology Research Institute (IITRI) submitted a proposal to the Air Force Space and Missile Systems Center (AF/SMC) detailing the replacement of a primary constituent common to their three white thermal-control coatings. The material of concern was *potassium silicate,* identified as "PS-7" and previously manufactured by Osram Sylvania. Economics had forced discontinued production of this material at Sylvania, which dictated that a replacement be found. This would then require that the coatings be reformulated using a new source of this raw material. These three coatings continue to be used on the vast majority of space vehicles today. At the time, roughly half a dozen programs at SMC used one or more of these paints. As part of their horizontal technology program, the SMC Chief Engineer's Office (SMC/EN) decided to fund this effort to ensure that these and other SMC SPOs would continue to have access to these paints. In 1991, funding was obtained for this effort and was included in an existing contract between IITRI and Wright Laboratory (WL). The work on this project was performed over a three-year period from Nov. 1991 through Oct. 1994. The scope of the work involved reformulation of the three IITRI white coatings—Z-93, YB-71, and S13GLO-1—and included extensive testing of the coatings' physical and optical properties. However, no funding was included to perform space radiation simulation testing, nor was there the capability at IITRI to perform such work. This report describes the test program that was implemented to evaluate the new formulations of the paints. The largest amount of testing was performed at The Aerospace Corporation, and this report presents the data from three separate space radiation exposure tests on approximately 80 test specimens. Pertinent data from other agencies (WL and NASA) is also included and discussed.

2. Background

Temperature regulation of satellites and launch vehicles is one of several technical problems that must be addressed by spacecraft designers and engineers.[1] The ultimate objective of thermal design is to ensure that the spacecraft operates within the prescribed temperature range defined by the temperature limitations of its subsystems, materials, and components. Spacecraft often rely on passive thermal control to maintain appropriate temperatures for their subsystems. Passive thermal control is a means of designing the subsystem with the proper thermal properties so that it balances the energy absorbed by the sun (either direct or Earth reflected) and the waste heat generated with the amount that can be radiated in order to achieve the desired temperature. The use of selectively reflecting surface coatings as an integral part of thermal design is one of the most common methods of passive thermal control. Outside of using mirrors, the best way to passively cool a spacecraft is by coating appropriate surfaces with a white paint. The optical properties of the paint allow the spacecraft to maintain proper temperatures to ensure the survival of the electronics. The important properties of a white paint are its solar absorptance, known as α_S (the percentage of solar radiation absorbed by the paint) and its emittance, known as ε (measure of ability to radiate heat). The ratio of these two quantities determines the surface temperature of the paint. For most spacecraft applications, a low α_S and a high ε are desired to achieve reasonable subsystem temperatures.

There are three IITRI white thermal control paints in use on spacecraft today: Z-93, YB-71, and S13GLO-1. The essential properties and composition of these paints are presented in Table 1. All were developed at IITRI[2–5] and have been used for years on DoD, civilian, and NASA spacecraft, and have a proven flight heritage. These paints were developed through an intensive program of raw material screening, processing, and testing. One of the most important aspects of their development and manufacture is the purity and consistency of the primary constituents. Two of these paints are ceramic and use potassium silicate as the binder; the third is a silicone-based paint. However, it does use potassium silicate to encapsulate the pigment. Until recently, all of these paints used Sylvania

Table 1. IITRI White Thermal Control Paints

	Z-93	YB-71	S13GLO-1
Composition	ZnO/K_2SiO_3	Zn_2TiO_4/K_2SiO_3	$ZnO(K_2SiO_3$ encapsulated)/Methyl Silicone
Pigment : Binder (wt.)	4.3:1	7.1:1	2.0:1
Solar Absorptance	0.15	0.13	0.20
Hemispherical Emittance	0.88	0.85	0.86
Cure time	7 days	14 days	7 days
Physical Characteristics	Slightly flexible, hard surface	Inflexible, very hard	Very flexible, soft surface
Outgassing: TML	1.5%	1.5%	0.2%
VCM	0	0	0.02%
Temperature Limit	700°C	900°C	300°C

PS-7, an electronic-grade potassium silicate, in their formulation. The problem with these paints occurred when Sylvania ceased production of PS-7. Acting on a proposal from IITRI, the Chief Engineer's Office funded a program at IITRI to identify a replacement potassium silicate for these paints and to reformulate or "clone" the three paints. Mr. Jerry Bauer of The Aerospace Corporation/Manufacturing Engineering Dept. was the technical monitor for the reformulation effort. Without this program, existing supplies of PS-7 for use in these paints would be exhausted in roughly two years. Programs that use these materials would be left without a flight-proven paint. Relying on a totally new paint system without flight heritage and/or an elaborate base of test data presents an unacceptable risk to most programs.

The major difficulty with white paints is that they do not retain their initial properties (high reflectance/low solar absorptance) when exposed to the natural space environment of vacuum, ultra-violet radiation, and charged-particle bombardment. Over the lifetime of the spacecraft, this exposure to ionizing radiation causes the paints to lose their high reflectance by developing radiation-induced absorptions within the pigment and/or binder. The net result of this radiation-induced absorption is a darkening (graying or browning) of the paint. This darkening causes the solar absorptance of the paint to increase and, thereby, causes the temperature of the painted surface to rise. Eventually this rise in temperature can become great enough to affect mission performance and/or spacecraft lifetime. A spacecraft designer or thermal engineer usually budgets for this end-of-life change in solar absorptance and sizes the radiating painted surfaces appropriately. To accomplish this task efficiently, the engineer must have accurate data on the end-of-life properties of the paint.[1]

The degradation of thermal control paints and coatings due to space exposure is well documented in the literature and has been the subject of much study for the last 30 years.[6] IITRI coatings have been well studied and are preferred for use on spacecraft because their optical properties are generally accepted as excellent and well known. Furthermore, their degradation in the space environment is less than other commercially available coatings and is generally somewhat predictable since flight data and a large amount of ground test data exist for these materials.[6] At the time that the coatings were developed, the raw materials used were the purest that could be obtained. Much of the work on thermal control paint stability has focused on material purity and the effect of these impurities on the production of radiation-induced absorptions or so-called "color centers." A replacement for PS-7 must not only have the appropriate physical and chemical properties of the original binder material, but must also yield a paint that performs similarly to the older version when exposed to the natural space radiation environment. Since impurity content will generally differ from one manufacturer to another, as well as from one process to another, tests are required to demonstrate that the new paints perform as well as the old. Analysis of the potassium silicate binder materials, while possibly illuminating, does not guarantee that the original and candidate replacement(s) will perform identically in a paint formulation. These factors must figure prominently in any program that attempts to replace a raw material in the paint formulations.

This program encompassed two separate efforts: (1) the reformulation of the three coatings with a replacement potassium silicate, and (2) evaluation and testing of the new coatings to requalify them for space use.

Identification of a replacement potassium silicate was the initial phase of the IITRI effort. Two other companies were considered as replacement vendors for this material—PQ Corporation, Philadelphia,

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PA, and Zaclon Industries Inc., Cleveland, OH. Table 2 lists the potassium silicate materials available from these vendors along with their specifications and those for Sylvania's PS-7. Candidate potassium silicate materials were evaluated against PS-7 for solids content, density, viscosity, pH, potassium-to-silicon ratio, trace impurities, and color. As can be seen from the data in Table 2, potassium silicate is a generic term for a family of chemicals with a wide range of chemical and physical properties. Potassium silicate glass is a colorless, super-cooled melt of potassium carbonate and pure silica sand. Potassium silicate solutions are prepared by dissolving potassium silicate glass in hot water. By varying the silica-to-potassium oxide ratio, products of definite but widely different properties are produced. It is customary in the silicates industry to express the concentration of the material in terms of its weight ratio. In the case of potassium silicate, this is expressed as SiO_2/K_2O. While the chemical formula for potassium silicate is K_2SiO_3, there are many structures of silicates that exist in solution.[7]

Zaclon was eliminated from consideration as a potential vendor due to a lack of guaranteed commitment to continue supplying their materials as advertised. PQ was then selected as the potential vendor, and reformulation studies were started with Z-93, using three potential candidate silicate materials: Kasil 1, Kasil 6, and Kasil 2130. Kasil 2135, the material most resembling PS-7, was unfortunately eliminated by IITRI due to lack of commitment for continued production at PQ. The three silicate materials, Kasil 2130, 2135, and 1624, are all electronic grade. However, the 2135 was considered experimental by PQ at that time. This is somewhat unfortunate since other paint manufacturers have elected to use this Kasil 2135 as a PS-7 replacement and have not encountered any significant difficulties with it. Kasil 1624, with its much different SiO_2/K_2O ratio, was not even considered as an alternative.

Based on the Z-93 studies, Kasil 6 was eliminated from further consideration since it produced coatings of high viscosity that were difficult to spray and cure. Additional work on the two remaining paints carried Kasil 1 and Kasil 2130 on through the reformulation effort. Based on the results from

Table 2. Potassium Silicate Specifications

Material	Mole ratio (SiO_2/K_2O)	Wt. Ratio (SiO_2/K_2O)	Weight % (K_2O)	Weight % (SiO_2)	Density (lb/gal)	Viscosity (centipoise)	pH	Clarity
PS-7	3.3		11	24	11.09	---	---	---
Kasil 1	3.92	2.5	8.3	20.8	10.5	40	11.3	clear liquid
Kasil 6	3.29	2.1	12.65	26.5	11.6	1050	11.7	clear liquid
Kasil 33	3.29	2.1	11.6	24.4	11.2	430	11.7	clear liquid
Kasil 2130	3.3	2.1	9.5	20	10.6	---	11.7	very clear
Kasil 2135	3.3	2.18	11	24	11	---	11.7	low viscosity,very clear
Kasil 1624	2.5	1.65	9.1	15	10.15	---	11.9	high solids, very clear
Zaclon #30	3.92	2.5	8.3	20.8	10.5	30	---	turbid liquid
Zaclon #200	3.25	2.07	9.42	19.5	10.6	5	---	filtered, clear water- white
Zaclon #865	3.33	2.1	12.45	26.25	11.6	325	---	filtered, clear water- white

these studies, the material chosen by IITRI as the replacement for PS-7 was Kasil 2130. Kasil 1 did show promise and was considered as a back-up material for Kasil 2130.

Both PS-7 and Kasil 2130 are rated as electronic-grade potassium silicates and therefore are analyzed for trace impurities by the manufacturer. Table 3 lists the manufacturer's specifications for these two materials.

The intent of the reformulation effort was to clone the original formulations of each paint. The three coatings were successfully reformulated with Kasil 2130, and each was designated with a "P" suffix to denote the PQ Kasil 2130 binder. IITRI prepared several batches of the three coatings along with samples of the older PS-7 versions for testing at various facilities. Several types of mechanical, optical, and space simulation tests were performed. These tests are listed below in Table 4 along with the agencies that performed the work:

Table 3. Manufacturer Specifications

Properties	PS-7	Kasil 2130
Total Solids	35.00±0.05	29.50±0.25
Mole ratio ($K_2O{:}SiO_2$)	1:3.30±0.05	---
% SiO_2/% K_2O	---	2.10±0.04
K_2O %	11.00±0.50	9.53±0.08
SiO_2 %	24.00±0.50	19.97±0.17
Specific Gravity	1.330±0.003	---
° Baume	---	30.9±0.3
Cu, ppm	0.05	0.5
Fe, ppm	30	30
Ti, ppm	---	0.3

Table 4. Paint Requalification Tests

Adhesion	Loral/Vought, IITRI
Abrasion resistance	IITRI
Density	IITRI
Viscosity	IITRI
Humidity	NASA/MSFC
Thermal cycling	NASA/MSFC
Solar Absorptance	Aerospace, NASA/MSFC, AZ Technology
Emittance	Aerospace, NASA/MSFC, NASA/GSFC
Torsion	Loral/Vought, IITRI
Sprayability	IITRI, Loral/Vought
Outgassing	Nusil Technology
Solar UV	NASA/GSFC
UV/Electrons	Aerospace, WL
UV/Atomic Oxygen	NASA/LeRC, NASA/MSFC, PPPL
Combined Effects	NASA/MSFC

3. Space Radiation Exposure Testing

One of the primary roles of The Aerospace Corporation in this program was to design and implement a plan that would address the issue of "space qualification" of the new paint formulations. To this end, there was a three-pronged approach taken to generate test data on space environmental exposure of the paints.

1. Encourage community participation in the requalification effort through specialized testing generated by the particular agencies (AF Labs, Contractors, NASA) interested in the outcome of the program. Test samples were provided to all interested parties by IITRI.

2. Perform limited large-scale space environmental exposure screening tests at The Aerospace Corporation on old and new formulations of the paints testing several samples of several batches of each paint for consistency.

3. Design an elaborate combined effects simulation test (UV, electrons, protons) to be performed at a well-characterized government/contractor facility.[8]

The reasons for this approach were several:

1. Generally, no one facility can perform a combined space environmental exposure test that includes all the parameters of concern. Thus, more than one type of test is usually required.

2. The more agencies participating in the program and running their particular test of interest, the more easily will the results of this program become acceptable to the spacecraft community.

3. Missions, and hence orbits, vary from one program to another and especially between the DoD and NASA. Generally speaking, the prime concern of the Air Force is geosynchronous missions, while NASA has a prime concern for low Earth orbit (LEO) missions. This results in a significant difference in the type of space environmental exposure required. For example, a geosynchronous mission involves exposure to high levels of charged particles (electrons, protons) of both high and low energies in addition to UV. There is no significant exposure to atomic oxygen. Conversely, a LEO mission generally involves insignificant exposure to charged particles, but usually has a significant to high exposure to atomic oxygen. In the case of elliptical orbit missions, the spacecraft can have exposure to all of the above. Figure 1 illustrates this point.

4. Several facilities can only expose a small number of samples at one time. Since exposure tests are generally run for a long time (>1000 h), data accumulation is slow.

ORBIT SPACE ENVIRONMENT PARAMETER	Terrestial	Low Earth 200 nmi (SHUTTLE)	Low Earth 425 nmi (DMSP)	GPS (11000 nmi)	Molniya 63° 12-hr Elliptical	Geosynchronous
Vacuum (torr)	none	1.4×10^{-9} 5.4×10^{-7}	6.5×10^{-11} 5.4×10^{-9}	$<10^{-12}$	varies	$< 10^{-14}$
Atomic Oxygen Flux $(cm^{-2}sec^{-1})$	negligible	10^{14}	10^{11}	negligible	varies	negligible
Solar X-rays, UV Visible and IR	filtered sun	one sun	one sun	one sun	one sun	one sun
Trapped Protons (Protons/ cm^2 /day)	———	———	2×10^9	4×10^{12}	3×10^9	2×10^{12}
Trapped Electrons (electrons/ cm^2 /day)	———	———	9×10^{10}	4×10^{12}	6×10^{11}	2×10^{12}
Solar Wind (electrons, protons, alpha particles/ cm^2 /sec)	none	none	none	none	$10^8 - 10^9$	$10^8 - 10^9$
Intermittent Solar Flares (protons/ cm^2 /sec)	negligible	negligible	negligible	10^4	10^5	10^5
Cosmic Rays (protons/ cm^2 /sec)	2-5	2-5	2-5	2-5	2-5	2-5

Figure 1. Space environment.

The Aerospace Corporation facilities can expose up to 40 one-inch samples at one time due to their large area beams. This allows assessment of batch-to-batch and sample-to-sample consistency. Running an elaborate test on only a few samples magnifies the uncertainty in such a test.

5. Optical properties measurements vary from one facility to another and need to be compared and perhaps averaged for good end-of-life numbers. Some facilities cannot measure optical properties, such as reflectance, in vacuum.

6. UV, electron, proton, or combined irradiation capabilities vary from one facility to another in the energies and fluxes that they use. This may reflect different orbital requirements as well as different testing methodologies.

7. Elaborate combined space environmental exposure tests are expensive and difficult to set up and run. Cost, schedule, and capability may not allow the best test to be performed.

Generally speaking, the plan was to let NASA perform the tests associated with atomic oxygen and/or UV, and to concentrate on the charged particle/UV tests at WL and The Aerospace Corporation. An elaborate combined space environment exposure test based on analytical modeling of energy deposition in the paints was designed at The Aerospace Corporation and set up to be run cooperatively at NASA/MSFC.[8]

4. Exposure Tests at Wright Laboratory

As part of the original arrangement for the reformulation/requalification program, Wright Laboratory (WL) and University of Dayton Research Institute (UDRI) agreed to perform limited space environmental exposure testing in their SCEPTRE facility.[9] This facility has the capability for exposure of five 1-inch specimens to UV and two electron beams simultaneously. The electron energies are adjustable up to 20 keV. The facility is set up to measure total hemispherical reflectance from 0.25 μm to 2.5 μm *in situ,* which allows a good determination of the changes in solar absorptance due to the radiation exposure. The significant shortcomings of the facility are the relatively low electron energies used and the inability to cool the samples. The low electron energies dictate that very shallow penetration of the paint will occur, and that the damage will be confined to the surface and may saturate quickly.[8] The optical thickness of the paints is appreciable; therefore, surface damage may not properly simulate the damage mechanisms encountered on orbit. The inability to cool the samples means that thermal degradation can occur along with radiation damage and produce excessive degradation in the samples.[6f,6m] Even so, comparing old and new versions of a paint side by side produces valuable information with respect to the success or failure of the reformulated paint's performance.

The first test performed at WL/UDRI[9] exposed samples of YB-71 and YB-71P, two each, along with a sample of Z-93. Two control samples were included in the chamber but were not exposed to radiation. The test lasted 1600 h at varying levels of UV intensity (1–3 sun level) and included 10 keV and 1 keV electrons (flux ratio 2:1) for a total fluence of 2.5×10^{16} electrons/cm^2. Reflectance measurements were performed before and after testing, and at intervals during the exposure. The data from this test is presented in Graph 1 in the Appendix. The pretest and post-test values for the solar absorptances for these samples along with their exposure conditions are shown in Table 5.

The data in Graph 1 illustrate the typical response of white thermal control paints to ionizing radiation. The solar absorptance of the sample is plotted as a function of the total solar exposure in equivalent UV sun hours. Since the electron exposure is simultaneous with the UV exposure, and is at a constant flux, the exposure time is also roughly a measure of electron dose. It is observed that the absorptance of the samples increases sharply during the early period of the test (< 500 EUVSH) and then levels off towards the end, as saturation is reached. However, two unexpected results are seen. First, the degradation of YB-71P samples is quite large and is much more than the YB-71. Second, the Z-93 shows much less degradation than the YB-71 or YB-71P samples. This data provided the

Table 5. Wright Laboratory Test 1

Paint	Batch #	Sun Intensity	EUVSH	Pretest α	Post-test α	Delta α
Z-93	---	3.0	3000	0.135	0.185	0.05
YB-71	R026	2.5	2500	0.087	0.232	0.145
YB-71	R026	1.6	1600	0.090	0.220	0.130
YB-71P	R028	2	2000	0.089	0.282	0.193
YB-71P	R028	2.7	2700	0.092	0.363	0.271

Exposure conditions: 1000 h, 1.66×10^{16} e$^-$/cm^2 @ 1 keV, 8.32×10^{15} e$^-$/cm^2 @ 10 keV

first indication that the YB-71P may have a problem when reformulated with the new Kasil 2130 binder material. Moreover, the test indicated that the more expensive paint, YB-71, which had been developed for lower solar absorptance,[4] and presumably greater radiation stability, did not perform as well as the inexpensive paint, Z-93.

This data caused enough concern that the test was re-run using the control samples from the first test and also including a sample of a different batch of YB-71P.[9] The results of this test are shown in Graph 2 and tabulated in Table 6. The results were basically the same as for the first test, with the exception that the different batches of YB-71P behaved similarly to the YB-71. This now indicated that there could be a batch problem with YB-71 and YB-71P (hereafter referred to as YB-71/P, meaning both, also Z-93/P and S13GLO-1/P when referring to both new and old versions of these paints) since samples from one batch consistently degraded more than samples from another batch. The magnitude of the degradation was also of some concern. Additional work performed on these samples by WL/UDRI is presented in the surface analysis section of this report.

Table 6 . WL Test 2

Paint	Batch #	Sun Intensity	EUVSH	Pretest α	Post-test α	Delta α
Z-93	---	1.2	1518	0.134	0.178	0.044
YB-71	R123	2.8	3542	0.097	0.297	0.200
YB-71P	R028	2.7	3416	0.106	0.419	0.313
YB-71P	S038	2.5	3163	0.093	0.266	0.173
YB-71P	S038	1.1	1392	0.097	0.233	0.136

Exposure conditions: 1265 h, 2.03 x 10^{16} e⁻/cm² @ 1 keV, 1.01 x 10^{16} e⁻/cm² @ 10 keV

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5. Initial Exposure Tests at The Aerospace Corporation

5.1   Paint Test 1

The data from WL on the YB-71/P caused enough concern that it was felt that limited testing at Aerospace should be initiated to confirm the results of the WL tests. Aerospace/Mechanics and Materials Technology Center has the capability for exposure of materials and components to space radiation. Two facilities with slightly different capabilities exist. For the first test of the paints, the smaller "NOMAD" (Nonmetallic & Optical Materials Annihilation Device) facility was used since it could give the best duplication of the test at WL. A schematic of the facility is shown in Figure 2.
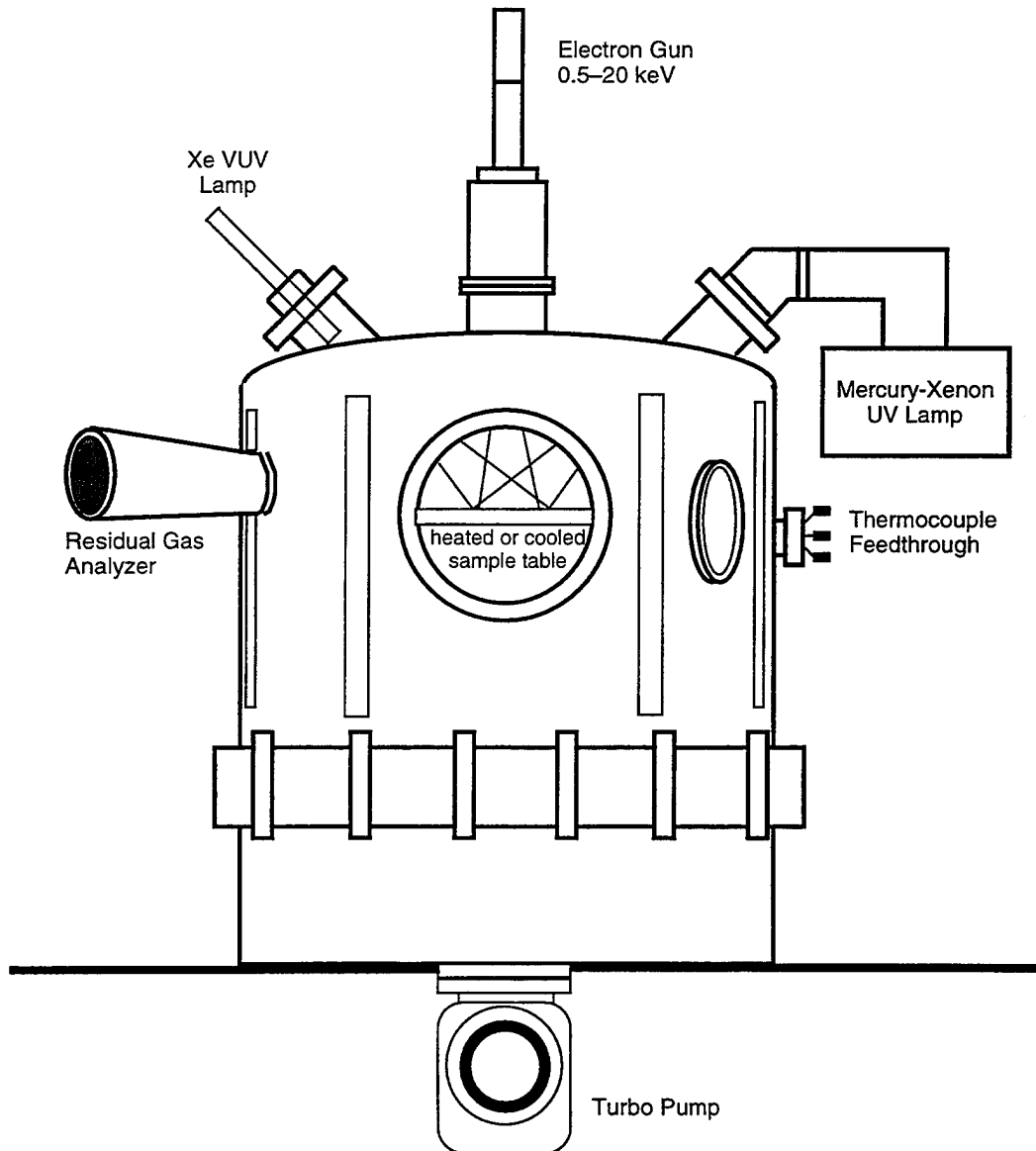
Figure 2. Nonmetallic & Optical Materials Annihilation Device (NOMAD).

The chamber is turbopumped with a base pressure of 1×10^{-9} torr and contains a sample table that can be heated (quartz/halogen lamp) or cooled with water or LN_2. Radiation sources included are a Hg(Xe) arc lamp for simulation of broadband UV, a xenon microwave discharge lamp for simulation of vacuum UV, and an electron flood gun capable of 1–20 keV electrons. The sources are configured to give overlapping beams with an exposure area of roughly 6×9 in. A data acquisition system records electron flux and fluence from Faraday cups, and temperature from thermocouples on the sample table. A video camera and recorder monitor the test. The major differences between this facility and the SCEPTRE facility at WL is the addition of water cooling for both the sample table and the UV source. Thus, the samples in the NOMAD test are held at roughly 16°C, while the sample temperature in the WL test can be as high as 100°C. The SCEPTRE facility has two electron flood guns for simultaneous exposure at two electron energies, while the NOMAD chamber has only one. Therefore, the electron exposures in this test were performed sequentially. The significant shortcoming of the NOMAD facility is the inability to measure reflectance of the samples *in situ*. Rather, samples must be exposed to a nitrogen gas backfill and quickly transported across the laboratory for a 12-min reflectance scan in air. The literature indicates that air recovery of radiation damage is minimized, delayed, slowed, or prevented by venting with an inert gas such as argon or nitrogen[6h, 6l] prior to air exposure.

The first Aerospace test was designed not only to duplicate the test from WL for confirmation of the results on YB-71/P, but also to expose samples of the other two paints as well to evaluate the performance of their new formulations. Since the facility has a relatively large exposure area, it was decided to test multiple samples and multiple batches where possible. All six paint formulations were tested at the same time; in this, way much more data was obtained from a single test.

The samples exposed in the first Aerospace paint test are described in Table 7 along with their pretest and post-test solar absorptances. The conditions of the exposure were as follows:

UV:	1150 h at 2.0 UV sun intensity (200–400nm) = 2300 EUVSH
Electrons:	$8.5 \times 10^{15}/cm^2$ at 10 keV and $17.5 \times 10^{15}/cm^2$ at 1 keV
Sample temperature:	12–20°C
Reflectance Measurement:	Perkin-Elmer Lambda-9 in air (after N_2 backfill, post-test)

The UV sun intensities were determined by measuring the spectral irradiance from 200 to 400 nm at various positions over the sample table with a calibrated spectroradiometer, and referencing the readings to the solar air mass zero curve. The beam homogeneity was within 20% of the 2.0 UV sun intensity. Only the Hg(Xe) arc lamp was used. Electron fluences were measured with three Faraday cups at various positions within the sample area. Beam homogeneity was adjusted with the focus controls on the gun power supply to within 10%. The layout of the samples is shown in Figure 3. Electron impingement is normal to the sample while the UV beam is approximately 30° off-normal.

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Table 7. Paint Test 1, Samples and Solar Absorptance Values

Paint	Batch #	Sample #	Pretest α	Post-test α	Delta α
Z-93	R009	#05	0.120	0.145	0.025
Z-93	R009	#12	(0.120)	0.145	0.025
Z-93P	R016	#06	0.125	0.157	0.032
Z-93P	S044	X-17	0.113	0.126	0.013
Z-93P	S044	X-18	(0.113)	0.148	0.035
S13GLO-1	Q090	MM-2	0.178	0.237	0.059
S13GPLO-1	R055	MM-84	0.145	0.227	0.082
S13GPLO-1	R055	MM-85	(0.145)	0.203	0.058
YB-71	R123	C015	0.090	0.135	0.045
YB-71	R123	C016	(0.090)	0.129	0.039
YB-71	R026	#01	0.122	0.199	0.077
YB-71P	R028	#02	0.107	0.229	0.122
YB-71P	R028	#11	(0.107)	0.227	0.120
YB-71P	S038	X-2	0.093	0.177	0.077

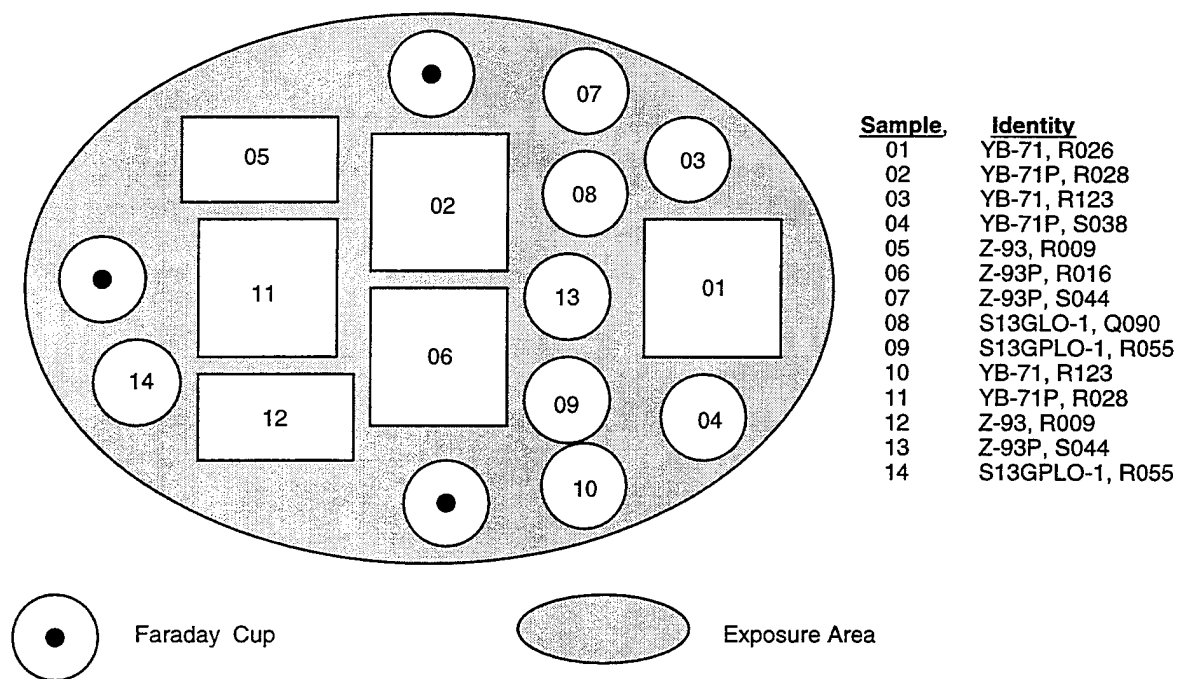| Sample,	Identity
01	YB-71, R026
02	YB-71P, R028
03	YB-71, R123
04	YB-71P, S038
05	Z-93, R009
06	Z-93P, R016
07	Z-93P, S044
08	S13GLO-1, Q090
09	S13GPLO-1, R055
10	YB-71, R123
11	YB-71P, R028
12	Z-93, R009
13	Z-93P, S044
14	S13GPLO-1, R055

Faraday Cup   Exposure Area

Figure 3. Sample layout for Paint Test 1.

The reflectance of the samples from 250–2500 nm was measured on a Perkin-Elmer Lambda-9 UV-VIS-NIR spectrometer using either a $BaSO_4$ or Halon-type integrating sphere. The reflectance curves were background-corrected and referenced to a NIST diffuse reflectance standard 2019d tile. Solar absorptance is calculated from the reflectance curve and referenced to the solar air mass zero curve. The solar absorptance number is thus valid only over the wavelength range of measurement: 250–2500 nm. *Since these paints absorb below 250 nm and beyond 2500 nm, the actual total solar absorptance increases by roughly 0.03.* However, the 250–2500 nm numbers will be used for consistent comparison between the Aerospace and WL/UDRI tests. All spectra were measured in air. For this test, the pretest spectrum was measured for only one sample of each batch. Where indicated, this spectrum was used as a reference for other post-test curves of different samples from the same batch. The post-test spectra were measured on the samples after the chamber had been vented with nitrogen. Exposure to air was minimized to prevent as much bleaching of the damage as possible. Results from WL/UDRI,[9] NASA/MSFC,[10] and NASA/LeRC[11] confirm that backfilling the chamber with N_2 can preservesmuch (about 90%) of the damage in these materials for several hours.

5.2   Results

Graphs 3–5 in the Appendix show typical temperature, electron flux, and fluence histories for the test. The sample table temperature cycles with the cooling tower temperature. The dose rate (flux) curve reflects the day-to-day adjustments of the electron gun. During a holiday shutdown with the UV and electron sources off, a failure of a vacuum pump briefly vented the system. Observation of the test specimens via video tape revealed little or no changes to the samples–those that were gray or brown remained gray or brown. The test was then resumed and completed after this shutdown period. Graphs 6-19 give the pretest and post-test reflectance curves for each test specimen. The post-test reflectance curve is displayed as the dashed line in all cases. Where no pretest measurement is available, the post-test curve is plotted against a companion sample from that batch as indicated.

A number in parentheses indicates that the value is that of the companion sample from the same batch. In later tests, each sample was measured prior to exposure. This data indicates that the degradation of the samples is significantly less than observed in the WL tests, particularly for the YB-71/P. The post-test solar absorptance comparisons indicate that Z-93 and Z-93P perform quite similarly, and that the degradation is slight. The delta numbers should be viewed with caution since some samples do not have a pretest measurement. Similarly, based on the data for the S13GLO-1/P samples, it would appear that the S13GLO-1 and S13GPLO-1 also behave comparably, but have more degradation than the Z-93/P. However, as in the WL tests, the post-test values for the YB-71 show a significant difference between batch R123 and R026, and that there is a difference between the two batches of YB-71P. Furthermore, there is significantly more degradation observed in the YB-71P samples. This data would then tend to confirm the earlier WL/UDRI results showing both a batch-to-batch problem with YB-71/P and that, generally, the YB-71P samples exhibit significantly more degradation than the YB-71. Another result from this data (and WL data) is the apparent superiority of Z-93/P over YB-71/P, a fact not in line with the folklore on these paints, but in line with recent data from LDEF.[12]

Inspection of the reflectance curves indicates that the radiation damage to Z-93/P produces increased absorption in the 400–700 nm region in the visible. Some increased reflectance occurs in the IR beyond 1400 nm due to water loss. Similar results are seen for the S13GLO-1/P samples. In some

cases, the entire absorption of the silicone binder is increased as it darkens. The damage to YB-71/P, however, seems to involve a broader bandwidth from 400 to 1200 nm, and in some samples, notably S038, sample X-2 and R028, samples #02 and #11, there is an absorption peak centered at 950 nm.

Generally, the post-test observations of the samples indicated that the Z-93/P appeared white, the S13GLO-1/P samples had become light tan, and the YB-71/P samples appeared gray.

The cause for the markedly less severe degradation of reflectance between the tests at WL and the tests at Aerospace is attributed to sample temperature. What effect the accidental venting of the chamber had on the samples is unknown, but the literature indicates that bleaching of damage in the infrared is the likely effect.[61] Since we normally do not observe degradation in the IR, this effect may be due to exposure to air. However, the main loss of reflectance in these materials is in the UV and visible where it affects the solar absorptance the most. The differences in reaction rate or defect diffusion rate at 16°C, as opposed to 100°C, are no doubt substantial and lead to increased degradation of the hot samples.[6f,6m] The major differences between the WL and Aerospace tests exist only for the YB-71/P samples since the post-test values and deltas for the Z-93 are reasonably close. This would suggest, as was also observed at WL, that backfilling the chamber with nitrogen prior to a rapid reflectance scan preserves most of the radiation-induced damage in these materials. The fact that similar results were obtained on similar samples suggests that this method of exposure and measurement is useful for screening tests, especially for batch-to-batch and sample-to-sample variability. However, for engineering numbers, measurements made in vacuum are preferred.

The results from both WL and Aerospace suggest strongly that there is some anomaly occurring with YB-71 and YB-71P. Both batch-to-batch, and old-to-new formulations produced inconsistent results when tested . Aerospace personnel inspected the records and batch cards at IITRI and found no clear reason for the poor performance of the R026 and R028 batches. However, during inspection of the records and processes at IITRI, three important points were brought out: (1) the pigment used for both YB-71/R026 and YB-71P/R028 was from the same batch (R027), possibly indicating a problem with the pigment in these two batches; (2) both batches were sprayed on the same day; and, (3), rust had been found in the nozzle of the spray gun that had been used to prepare these test specimens. This information was particularly important since rust-like spots had appeared on sample #01 (YB-71/R026) during the test exposure.

A set of samples, now referred to a batch T081, was resprayed with a retained portion of batch R028 and included in the next test in order to answer the question of contamination during the spraying of R026/R028. IITRI batch numbers reflect the year that the material was produced. The letter "R" refers to 1993, and "T" is 1994. The batch card indicates the date a process was performed, such as a pigment synthesis, binder synthesis, or sample/component spraying. Thus, it is necessary to track all components in a paint from the batch card since the components were produced at different times. Samples from T081 were sprayed in 1994, but they were blended in 1993, and the pigment used for this batch (R027) was produced earlier. Several separate batches of ZOT pigment were blended to make the final batch of pigment used in R026/R028/T081.

Analyses were performed on samples of both PS-7 and Kasil 2130 in an attempt to find a significant difference between the two materials that could account for the difference in performance. Similarly,

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since the two bad batches, R026 and R028, both used the same pigment, analyses were also performed on these and other lots of pigment in an attempt to find a difference in pigment composition that could be related to performance.

6. Pigment/Binder Analyses

Spectrographic analysis of both Sylvania PS-7 and PQ Kasil 2130 was performed using Optical Emission Spectroscopy. This technique determines the elemental composition of a sample from the X-ray emissions produced during ashing, and is semiquantitative. The results of the analysis are shown in Table 8. It is apparent from this data that while the manufacturers of the materials claim potassium and silicon percentages of 24:20 and 11:10, this method does not produce these ratios. However, when the titrimetric methods used and recommended by PQ were employed, the correct values were obtained, and the materials have nearly identical K:Si ratios.[13] Examination of the trace elements in these silicate samples indicates that except for a 10-fold increase in Ca in the PS-7 relative to the Kasil 2130, the materials are nearly identical. However, one has to ask if the difference between 10 and 100 ppm calcium is significant.

Ion Microprobe Mass Spectrometry (IMMA) examination of the two silicates uncovered traces of Li and B in the Kasil 2130. From the results of the spectrographic study, it appears that the concentration of these elements is less than about 20 ppm. Note that for both materials, the Fe and Cu concentrations are above the manufacturer's quoted limits (See Table 3).

Thus, analysis of these silicates has indicated that the Kasil 2130 material has traces of Li and B, while the PS-7 has ten times the calcium concentration. Whether these differences can account for the different responses of the YB-71/P is purely speculative. Various batches of zinc orthotitanate (ZOT) pigments used for manufacture of YB-71/P batches R026 and R028, as well as other batches, were also analyzed by Optical Emission Spectroscopy. The results of this study are shown in Table 9. The analysis shows that there are very small amounts of Al, Ca, Cu, Mg, and Si in these materials, but that their content appears random and does not correlate with samples of paint that have shown poor performance in testing. The values for Zn and Ti should be noted with caution since the pigments are known to contain varying small amounts of ZnO.[13]

Table 8. Analysis of Potassium Silicates

Element	PS-7 %	Kasil 2130 %
Si	9.2	11
K	20	14
Mg	0.00035	0.00079
Fe	0.0079	0.0079
Al	0.0024	0.0047
V	0.0030	0.0012
Cu	0.00025	0.00018
Na	0.048	0.031
Ti	0.0032	0.0051
Ca	0.011	0.00093
B	<0.002	<0.002
Li	<0.001	<0.001
Other	nil	nil

Table 9. ZOT Pigment Analysis

Sample	Zn	Ti	Zn :Ti	Mg	Si	Cu	Al	Ca
93942A	81	14	5.79	0.0012	0.0054	<0.00005	0.0073	0.0062
93942B[+]	75	8.5	8.82	0.00056	0.0018	<0.00005	<0.001	0.0025
86366A	66	9.2	7.17	0.00036	<0.001	<0.00005	<0.001	0.0023
86366B*	70	14	5.00	0.0002	<0.001	<0.00005	<0.001	0.0016
89902A	61	11	5.55	0.00037	<0.001	0.00026	<0.001	0.0019
89902B*	60	18	3.33	0.00049	<0.001	0.00013	<0.001	0.0027
87578B	57	19	3.00	0.00043	0.0032	<0.00005	<0.001	0.0031
59902A	65	26	2.50	0.0011	0.0094	<0.00005	<0.001	0.0059
76366A	65	9.5	6.84	0.0004	<0.001	<0.00005	<0.001	0.0026
54142	55	17	3.24	0.00065	<0.001	<0.00005	<0.001	0.0013
51518	62	18	3.44	0.0012	<0.001	<0.00005	0.0096	0.0029
73538A	61	13	4.69	0.0007	<0.001	<0.00005	0.0062	0.0034

* refers to R027 pigment used for R026/R028, [+] refers to pigment used for R123.

Ignoring the widely varying Zn:Ti ratio, it can be seen that the pigments contain about 2–12 ppm Mg, less than 100 ppm Si, less than 3 ppm Cu, less than 100 ppm Al, and 13–62 ppm Ca. Other elements were not detected. The theoretical wt. ratio for Zn_2TiO_4 is 2.73, and for ZnO it is 4.09. ZnO is present because a deliberate excess is used in the ZOT manufacture.[13] Thus, numbers greater than 4.09 or less than 2.73 are suspect. In fact, the utility of this set of data for this ratio, as well as for the concentrations of small impurities, is somewhat questionable. Conclusions based on the Zn:Ti ratio or small changes in very minor impurities such as these are not warranted. However, it is clear that there are no significant impurities in the ZOT pigments as processed by IITRI.

Since the ratio of Zn to Ti seems to vary widely by the spectrographic analysis, X-ray Crystallography was performed on these same pigment samples. The results indicate that the crystalline pigments are primarily α-cubic zinc orthotitanate and contain small amounts of ZnO (1–2%). One sample, 73538A, showed a small amount of zinc metatitanate, $ZnTiO_3$. However, this sample was not from any pigment batch used in this requalification program. Thus, the reasons for the wide variance in the Zn:Ti ratio in the spectrographic analysis are unclear. However, the results here consistently indicate that the pigments are fairly pure materials.

The results of these analyses do not shed any light on whether the problem with the YB-71/P is due to the pigment or the binder. If there is a significant impurity in the Kasil 2130 that causes the YB-71P versions to perform poorly, it has not been found. Similarly, no significant differences have been found in the batches of pigment that would suggest a reason for the poor performance of some paint batches. We do not believe it likely that very small amounts of B, Li, or Ca in the silicate are of significance. Similarly, the very small impurity content of the pigments is also not significant. The widely varying and unrealistic Zn:Ti ratios are puzzling and not in line with the values obtained by other methods.

7. Extended Exposure Tests at The Aerospace Corporation

Since both pigment and binder analyses failed to produce any conclusive evidence as to the reason for the difference in performance between YB-71 and YB-71P, it was decided to perform a large-scale screening test to evaluate many samples of YB-71 and YB-71P from several batches. In addition, since bad lots of pigment could not be ruled out as the cause of the degradation and since a batch of YB-71 containing a suspected bad pigment (same as used in R026/R028) had been sold to Aerojet for use on the DSP sensor, witness samples from this batch stored at Aerojet were obtained and included in the second test. Additionally, IITRI had in storage some samples from the 80's that we wished to evaluate to investigate storage, aging, and contamination effects, as well as process and quality control.

7.1   ZOT Test

This test was initially started in the NOMAD facility and run for roughly 350 h while the samples were exposed to the 10 keV electrons (8.5×10^{15}/cm^2). However, failure of the turbopump produced not only a loss of vacuum but a burnout of the electron gun. This necessitated a restart of the test in another chamber. The samples were then removed from the NOMAD chamber and exposed to air for 3 days while another facility, the "Deathstar," was prepared for continuation or restart of the test. No visible damage was seen on the samples due to this 350-h UV and electron exposure. Figure 4 shows the layout and capabilities of the "Deathstar" facility. It is similar to but has more robust capabilities than the NOMAD facility and consists of a larger chamber and sample table, as well as incorporating larger-area UV and electron beams. The "Deathstar" uses a xenon arc lamp for
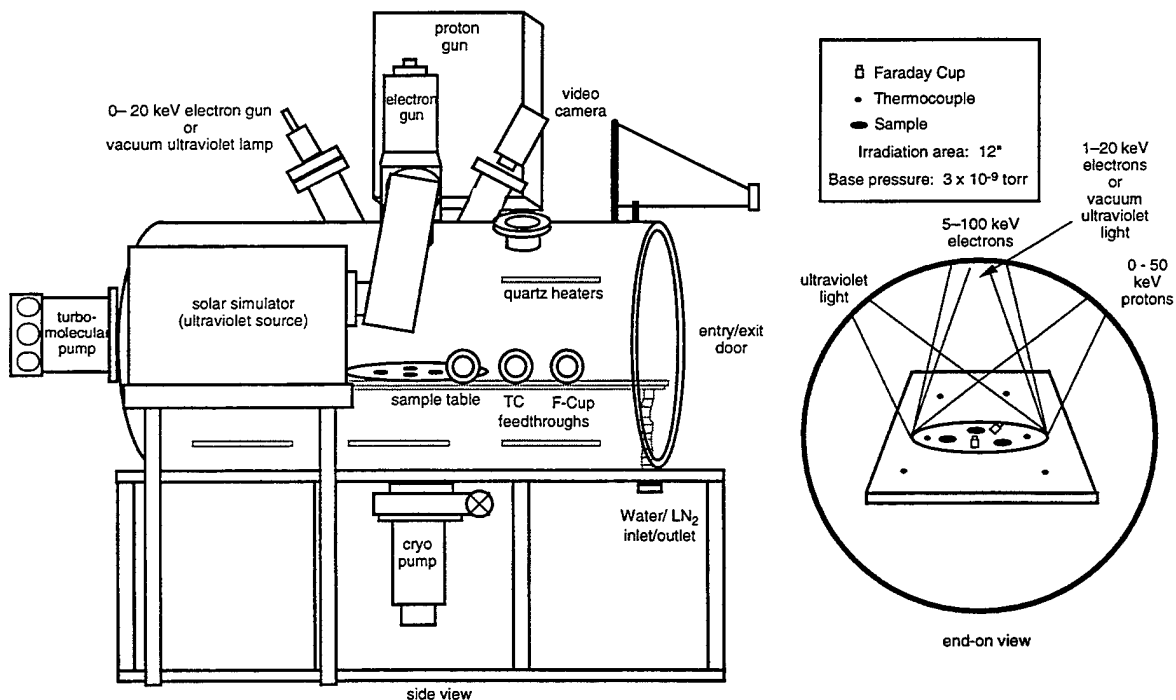

Figure 4. "Deathstar" space environment effects chamber.

solar simulation and has an electron gun capable of up to 120-keV electrons. Since the degradation of the paints in the first paint test was small, and since it is believed that very low energy electrons (1–10 keV) produce shallow surface damage that saturates quickly, it was decided to run this test using 40-keV electrons for deeper penetration into the paint.[6n] It was felt that in order to obtain useful and unambiguous data on the *relative* performance of the paint samples, they should be exposed until visible damage occurred. The conditions for the test are presented below.

UV:	1233 h at 2.10 UV sun intensity (200–400 nm) = 2589 EUVSH
Electrons:	3.1×10^{16} e-/m^2 at 40 keV @ 6 $\times 10^9$ e-/cm^2 s
Sample temperature:	22–27°C
Reflectance Measurement:	Lambda-9 in air (after N$_2$ backfield, post-test)

7.2   Results

The sample layout is presented in Figure 5. Graphs 20-22 in the Appendix give the sample temperature, electron flux history, and total electron fluence. A temporary outage of the cooling tower necessitated shutting off the UV and electron sources for a weekend. The higher than normal sample temperatures early in the test reflect this outage. However, the samples remained in vacuum during this off period. The sample complement and solar absorptance values are shown in Table 10.

Table 10. ZOT Test Samples and Solar Absorptance Values

Paint	Batch #	Sample #	Pretest α	Post-test α	Delta α
YB-71	P062	#2	0.093	0.201	0.108
YB-71	Q051	#1	0.103	0.199	0.096
YB-71	Q051	#2	0.105	0.200	0.095
YB-71	R123	C001	0.082	0.211	0.129
YB-71	R123	C014	0.079	0.224	0.145
YB-71	R026	#2	0.137	0.312	0.175
YB-71	R026	#3	0.125	0.319	0.194
YB-71P	R028	#5	0.102	0.377	0.275
YB-71P	R028	#6	0.107	0.376	0.269
YB-71P	S038	X-7	0.093	0.300	0.207
YB-71P	S038	X-8	0.088	0.309	0.221
YB-71P	S038	X-9	0.088	0.299	0.211
YB-71P	S081	A-12	0.070	0.393	0.323
YB-71P	S081	A-18	0.073	0.378	0.305
YB-71P	T081	B098	0.100	0.338	0.238
YB-71P	T081	B099	0.101	0.336	0.235
Z-93	G028	#2	0.139	0.192	0.053
Z-93	G028	#3	0.133	0.222	0.089
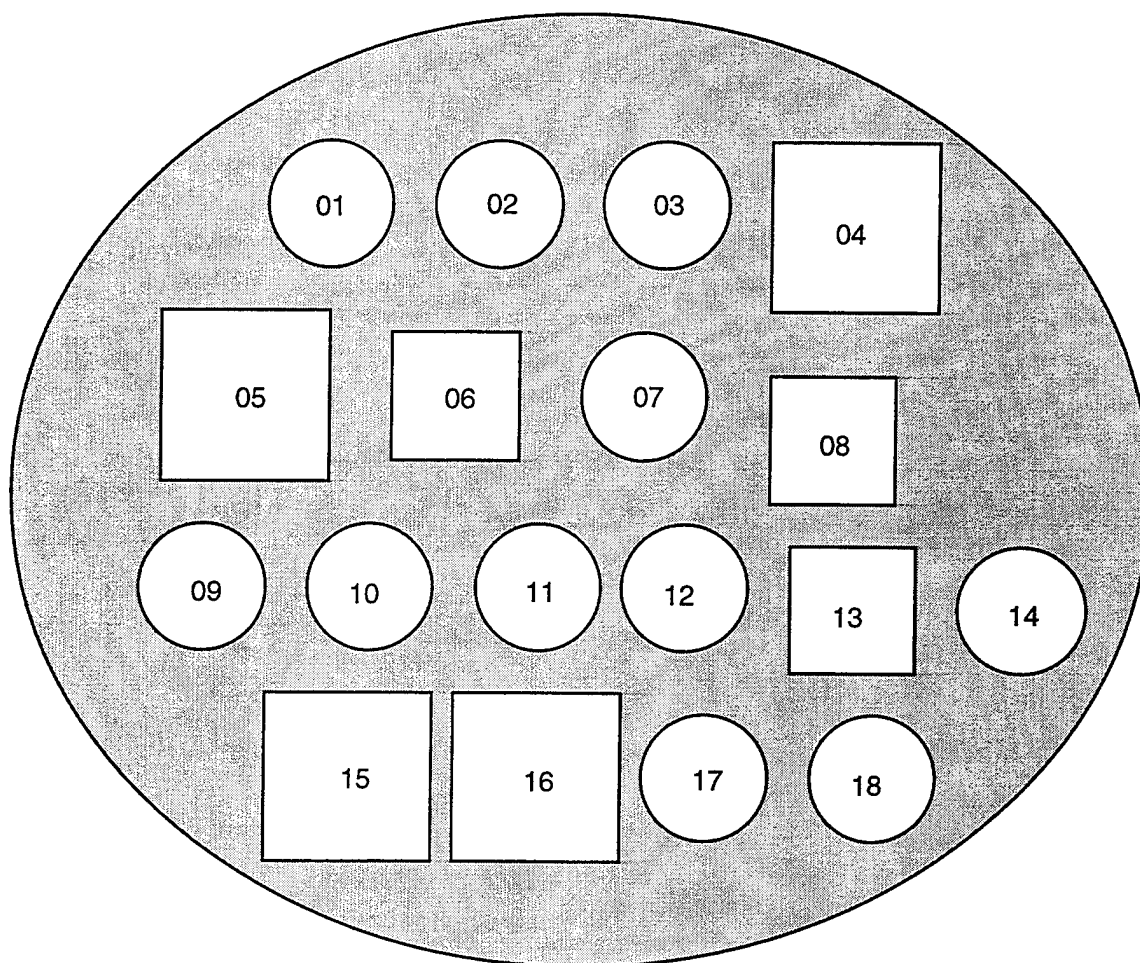
Sample #	Identity		Sample #	Identity
01	YB-71P, S038		10	YB-71P, S038
02	YP-71P, T081		11	YB-71P, S081
03	Z-93, G028		12	YB-71, R123
04	YB-71, R026		13	YB-71, P062
05	YB-71, R026		14	YB-71P, T081
06	YB-71P, S081		15	YB-71P, R028
08	YB-71, Q051		16	YB-71P, R028
09	Z-93, G028		17	YB-71, R123
			18	YB-71P, S038

Figure 5. Sample layout for ZOT test.

All samples were measured pretest, which allows direct comparison of the delta α numbers. The Z-93 samples were used as controls to assess the differences between this test and the previous run. It becomes apparent that the increased magnitude of the degradation observed in the Z-93 samples indicates that this was a more severe environment than the first paint test.[6n] The values for the post-test and delta α are comparable to those obtained by WL/UDRI (See Tables 5 and 6 for comparison).

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Graphs 23–40 in the Appendix give the pretest and post-test reflectance curves for each sample. The post-test curve is indicated by the dashed line. Inspection, side by side, indicated that the test samples were markedly "grayer" than the controls.

Several conclusions can be drawn from this data:

1. The YP-71P samples show significantly greater degradation than the YB-71 samples.

2. Within a batch, degradation appears consistent and reproducible.

3. YB-71 batch R026 exhibits substantially more degradation than the other batches of YB-71.

4. The older batches of YB-71 appear more stable relative to the more recent batches.

5. Batch T081 performed similarly to R028, eliminating possible spray-gun contamination as a cause of the poor paint batch performance.

6. The reflectance curves of YB-71 show an absorption between 400 and 1200 nm that is different than that observed for the YB-71P samples.

The solar absorptance data from this test is presented in bargraph format in Graph 41, dramatically illustrating the above points 1 through 5. Comparison of Graphs 42 and 43 illustrate point 6. Graph 42 plots the post-test curves of all YB-71 samples tested and how the reflectance degrades between 400 and 1500 nm. The batch consistency is clear from this data as well as the anomalous results from batch R026. Graph 43 plots the data from all the YB-71P samples tested and indicates that the shape of the reflectance curve between 400 and 1500 nm is consistently different in the "P" samples relative to the older formulations. Batch consistency is also apparent from this data. A tentative hypothesis for this difference in reflectance spectra is that in the "P" versions there is a reduction of Ti^{+4} to Ti^{+3} that produces the absorption centered at 950 nm.[14] In the older formulations, the reduction does not occur as readily; hence, the absorption at 950 nm is not as prominent. However, there appears to be an absorption around 600–650 nm, which may be due to a reduction of Zn^{+2} to Zn^{+1}, or to interstitial Zn.[6m] The relative rates between these two processes appear to be different in the two formulations. It seems reasonable to assume that some unknown component of the Kasil 2130 is responsible for this phenomenon, promoting the reduction of Ti^{+4}.

This screening type of approach gave such useful data for YB-71/P that it was decided to press on with a third test to evaluate batch-to-batch and sample-to-sample performance for Z-93/P and S13GLO-1/P.

7.3   Paint Test 2

The samples included in this test are shown in Table 11. In addition to the Z-93/P and S13GLO-1/P complement, samples of Z-93K and YB-71K were included to evaluate the performance of the Kasil 1 binder (-K denotes Kasil 1). Samples of YB-71 and some heat-treated YB-71P from batch T081

Table 11. Paint Test 2 Samples and Solar Absorptance Values

Paint	Batch #	Sample #	Pretest α	Post-test α	Delta α
Z-93	G028	#61	0.138	0.174	0.036
Z-93	G028	#62	0.134	0.168	0.034
Z-93	R115	A002	0.109	0.145	0.036
Z-93	R115	A046	0.110	0.145	0.035
Z-93	S044	X-32	0.107	0.154	0.047
Z-93	S044	X-39	0.109	0.142	0.033
Z-93P	R016	#R	0.111	0.176	0.065
Z-93P	R120	A094	0.108	0.131	0.023
Z-93P	R120	A110	0.110	0.142	0.032
Z-93P	S044	X-12	0.108	0.176	0.068
Z-93P	S044	X-15	0.108	0.147	0.039
Z-93P	S044	X-22	0.109	0.140	0.031
Z-93K	R121	A028	0.116	0.144	0.028
Z-93K	R052	MM54	0.137	0.163	0.026
Z-93K	R052	MM63	0.139	0.151	0.012
S13GLO-1	S174	X-36	0.161	0.287	0.126
S13GLO-1	S174	X-37	0.154	0.275	0.121
S13GLO-1	S174	X-38	0.156	0.272	0.116
S13GLO-1	T114	CH-1	0.175	0.306	0.131
S13GLO-1	T114	CH-2	0.177	0.301	0.124
S13GLO-1	T114	CH-4	0.172	0.280	0.108
S13GPLO-1	R055	MM-77	0.143	0.484	0.341
S13GPLO-1	R055	MM-81	0.143	0.428	0.285
S13GPLO-1	R055	MM-86	0.141	0.457	0.316
S13GPLO-1	R055	#0	0.146	0.406	0.260
S13GPLO-1	S174	Y-37	0.157	0.298	0.141
S13GPLO-1	S174	Y-38	0.160	0.272	0.112
S13GPLO-1	S174	Y-39	0.161	0.297	0.136
YB-71/Z-93	G032	#0	0.105	0.161	0.056
YB-71/Z-93	G032	#9	0.102	0.152	0.050
YB-71P/HT	T081	B-83	0.091	0.199	0.108
YB-71P/HT	T081	B-84	0.094	0.216	0.122
YB-71P	T081	B-97	0.087	0.325	0.238
YB-71K	R053	MM-60	0.118	0.316	0.198

YB-71P/HT samples were heated in air for 3 h at 400°C.

were also exposed to evaluate an IITRI solution claiming that heat treatment in air should decrease the degradation of the paint.[13]

The test was run in the "Deathstar" facility and conditions, which were nearly the same as for the ZOT Test, are shown below.

UV:	1226 h at 2.10 UV sun intensity (200–400 nm) = 2575 EUVSH
Electrons:	3.0×10^{16} e⁻/m² at 40 keV @ 6×10^9 e⁻/cm²s
Sample temperature:	22 -29 °C
Reflectance Measurement:	Lambda-9 in air (after N_2 backfill, post-test)

Sample layout was quite similar to that used in the ZOT Test, and utilized hexagonal close packing to expose this larger number of samples.

7.4   Results

As before, the test parameters, such as sample temperature, electron flux, and fluence, are given in Graphs 44–46 in the Appendix. The sample reflectance curves are shown in Graphs 47–80. The post-test reflectance curve is indicated by the dashed line. The Z-93/P specimens generally appeared white or slightly yellow. The YB-71/P samples were either white or gray, while the S13GLO-1/P samples were brown or tan. The complete set of samples from batch R055 (S13GPLO-1) developed black lines early in the test, and these marks continued to become more prominent as the exposure continued. These samples were a darker brown than other samples. The reasons for this are unknown, but strongly indicate some sort of batch problem with the S13GLO-1/P as well. It may be the result of sample charging and/or arcing at the higher electron voltage used in this test relative to WL and Paint Test 1.

For the Z-93/P/K samples, the results from this exposure are comparable to the data obtained in Paint Test 1 and also that from WL/UDRI. The larger data set in this test obviously provides more information on trends and batch-to-batch and sample-to-sample variations.

The pretest values for Z-93 are fairly consistent, with batch G028 somewhat higher than the others (R115 and S044). This batch was made in 1981 and may reflect older processing conditions or storage and aging effects of this paint. Generally, as the paints dry out with time or in vacuum, they increase in reflectance. The post-test values follow this trend, with the G028 batch correspondingly higher in absorptance. Thus, the delta α values are remarkably consistent, with only one sample of batch S044 being somewhat higher in post-test reflectance. WL/UDRI obtained slightly higher values, as shown previously in Tables 1 and 2. However, the batches used for these tests are not known but are probably different from those tested here. The numbers are in the same range as obtained in this test. Smaller changes in α were obtained in Paint Test 1, as shown in Table 7. This may be due to the lower-energy electrons used, as well as the slightly lower temperature (16°C compared to 25°C) in that test.

The Z-93P samples all show remarkable consistency in pretest reflectance; however, there are some differences in post-test values and the delta α numbers as well. The values for pretest, post-test, and delta α all compare favorably with those obtained in Paint Test 1. The one sample from batch R016 showed somewhat higher degradation, as did one sample of batch S044. One sample of batch R120

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was significantly lower in post-test and delta. However, in general, the values obtained for the Z-93P samples indicate very similar behavior to the Z-93 samples. This corroborates the tentative conclusion regarding Z-93/P from Paint Test 1; that is, substitution of Kasil 2130 for PS-7 in Z-93 produces a nearly identical material.

The Z-93K samples indicated some significant differences in pretest reflectance between batches. There are significant differences in post-test reflectance as well that lead to a mixed set of values for delta α. Generally though, the values for delta α are slightly less for the "K" materials as opposed to the P, or the older Z-93. Still, Z-93K is not considered a viable material since it is much more fragile than the other paints and has significant adhesion problems as well. The Z-93K samples exhibited cracking and delamination during vacuum dryout. Samples of Z-93K and YB-71K that were placed in the test chamber and pumped on overnight prior to beginning the irradiation suffered delamination and cracking and were replaced with companion samples from the same batches. Even so, these replacement samples showed cracking and delamination during the test. A sample of Z-93P also cracked as the test exposure proceeded. A photograph of this sample is shown in Figure 6. This damage is typical of that observed in these paints.

Figure 6.   Optical micrograph of cracked surface of Z-93P, batch R120, sample A094, 6.3× magnification.

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The two batches of S13GLO-1 tested showed similar behavior with some minor differences. The pretest data indicates that batch S174 is a slightly whiter material than the T114 batch and that both batches gave consistent pretest values among the samples for that batch. The post-test values do indicate some slight scatter, but are consistent and lead to similar numbers for the delta α of this paint. When compared to the one sample of S13GLO-1 tested in Paint Test 1, the values here are higher by about a factor of 2 for the delta, with the pretest numbers being comparable.

The S13GPLO-1 test set consisted of two batches, and different results were observed with each. The R055 batch exhibited a slightly lower solar absorptance pretest than the S174 batch, and the values for samples within a batch are fairly consistent. Of major concern, however, is the difference in response of the two batches . The R055 batch gave values roughly 50–60% higher in absorptance than the S174 samples. This translates to almost a factor of 2 in delta α between the two batches. The reasons for this are obvious, but not understood. All four samples of the R055 batch exhibited dark streaks and blacks lines early in the test, possibly due to arcing of the sample from charging. Figure 7 is a photograph of one of the samples from batch R055. At 32×, the streaks appear as a gray mottling
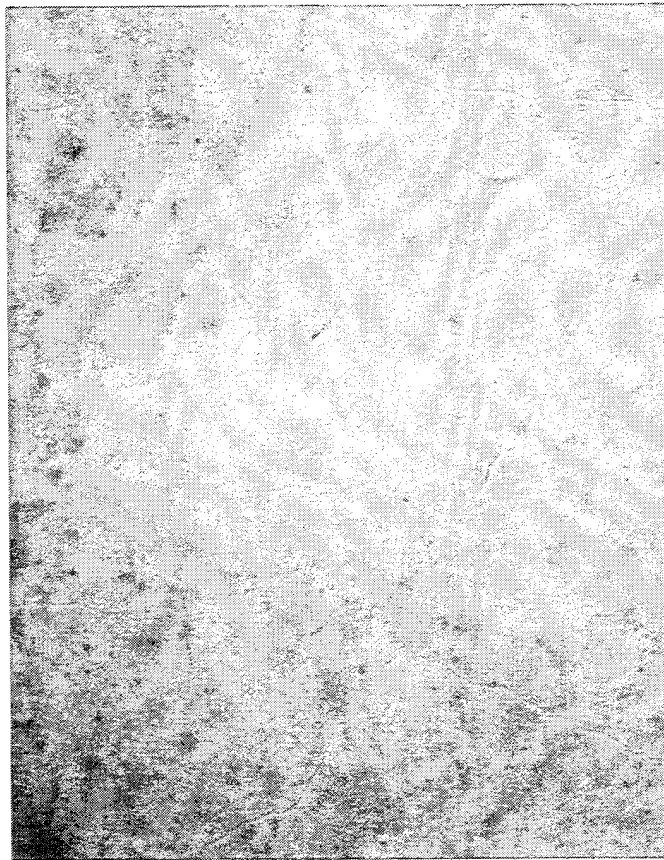
Figure 7.   Optical micrograph of mottled and discolored surface of
            S13GPLO-1, batch R055, sample MM-77, 32× magnification.

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over the brown sample. Why this is not observed in Paint Test 1 is attributed to the difference in electron energy; the higher 40 keV electrons cause more intense charging and arc-over than the 10 and 1 keV electrons. The values for batch R055 from Paint Test 1 in Table 7 were roughly half the post-test absorptance of the samples in Paint Test 2. Clearly, the higher keV electrons produce more damage in the material. Since higher electron (and for that matter, proton) energies and fluxes exist for on-orbit conditions, these results should not be ignored.

These results indicate that for one batch of S13GPLO-1 (S174) the results are very similar to the S13GLO-1 samples. The R055 batch showed much higher degradation. One would expect that of all the paints tested in this program the S13 materials would behave similarly since the degradation of this paint is dominated by the darkening of the silicone binder, and the potassium silicate is a very minor component of the paint. The cause of the anomalous results for batch R055 is not understood at this time.

The relatively small number of YB-71/P/K samples exposed in Paint Test 2 produced some interest-ing results. The YB-71 from 1981, batch G032, showed remarkable stability with a delta α of only 0.05–0.06, even better than the P062 and Q051 batches tested previously. This continues the trend of demonstrating that the older YB-71 materials produced by IITRI are the most stable. This raises the concern that small unrecognized changes in YB-71 processing and manufacture might be part of the cause of the problem. Samples of YB-71P that had been heat treated in air at 400°C for 3 h were also exposed with a companion sample that did not receive such treatment. The two heat-treated samples showed major improvements in stability, their degradation being only half that of the untreated sam-ple. As expected, the heat-treated samples also showed improvements in pretest reflectance, probably due to water loss, as well as bleaching of nonstoichiometric defects inherent in the material. The one sample of YB-71K gave the most interesting results by developing a large blue-gray spot in the center of the sample. The post-test reflectance of the sample was similar to the untreated YB-71P; however, the shape of the curve was more similar to YB-71, showing absorption at about 500 nm in addition to the appearance of the peak at 950 nm.

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8. Surface Analysis of YB-71/P Samples

A subset of the paint samples irradiated at The Aerospace Corporation and appropriate "pretest" samples were analyzed by X-ray Photoelectron Spectroscopy (XPS). Particular emphasis was placed on the YB-71P reformulated coating, which did not perform as well as the original YB-71 formulation. A comparison of these results will be made with XPS analyses of paint samples tested at WL/UDRI Space Combined Effects Primary Test and Research Equipment (SCEPTRE) Facility, operated by the University of Dayton Research Institute (UDRI). It has been reported[8] that the poor performance YB-71P coatings possessed significantly higher surface K:Si atom ratios than the theoretical value of 0.6061. It was hypothesized by Cerbus and Carlin,[9] on the basis of the UDRI XPS results, that the excess potassium is the cause of the increased degradation of the coatings upon UV/electron irradiation.

Table 12 lists the samples analyzed by XPS, and their exposure conditions.

Table 12. White Thermal Control Samples Analyzed by XPS

Coating	Batch	Sample No.	Surface	Pigment	Binder	Exposure
YB-71P	T081	B-94/7.3 mils	Pretest	ZOT	Kasil 2130	
	(R028)	B-98/7.5 mils	Post-test	ZOT	Kasil 2130	1
		B-99/8.2 mils	Post-test	ZOT	Kasil 2130	1
YB-71P	S038	X-4	Pretest	ZOT	Kasil 2130	
		X-7	Post-test	ZOT	Kasil 2130	1
		X-8	Post-test	ZOT	Kasil 2130	1
		X-9	Post-test	ZOT	Kasil 2130	1
YB-71P	S081	A17	Pretest	ZOT	Kasil 2130	
		A12	Post-test	ZOT	Kasil 2130	1
		A18	Post-test	ZOT	Kasil 2130	1
YB-71K	R023	MM57	Pretest	ZOT	Kasil #1	
		MM60	Post-test	ZOT	Kasil #1	2
YB-71	R123	C-001	Post-test	ZOT	PS-7	1
		C-014	Post-test	ZOT	PS-7	1
YB-71	Q051	#3	Pretest	ZOT	PS-7	
		#4	Post-test	ZOT	PS-7	
		#2	Post-test	ZOT	PS-7	1
YB-71	P062	#1	Pretest	ZOT	PS-7	
		#3	Pretest	ZOT	PS-7	
		#2	Post-test	ZOT	PS-7	1
YB-71	?	10/16/90	Pretest	ZOT	PS-7	
Z93	G028	#2	Post-test	ZnO	PS-7	1
		#3	Post-test	ZnO	PS-7	1

(1) ZOT Test	• Water filtered Xe lamp: 1233 h at 2.1 sun intensity, 2589 EUVSH
	• 40 keV electrons: 6×10^9 electrons/sq. cm flux, 3.1×10^{16} fluence
	• Samples water cooled: backside temperature 22-27 °C
(2) Paint Test 2	• Water filtered Xe lamp: 1226 hours at 2.1 sun intensity, 2575 EUVSH
	• 40 keV electrons: 6×10^9 electrons/sq. cm flux, 3.0×10^{16} fluence
	• Samples water cooled: backside temperature 22-29 °C

8.1   XPS Methods

The white thermal coating samples were analyzed by XPS using a VG Scientific LTD ESCALAB MK II instrument. The samples were mounted on sample stubs with double-sided tape. Survey scans from 0 to 1100 eV binding energy were acquired with an Al-Kα source to qualitatively determine the sample surface composition. Analysis areas were about 4 mm × 5 mm in size, and analysis depth was about 50–100Å. High-resolution elemental scans were subsequently run to obtain semi-quantitative elemental analyses from peak area measurements and chemical state information from the details of binding energy and shape. Measured peak areas for all detected elements were corrected by elemental sensitivity factors before normalization to give surface atom %. The quantization error on a relative basis is ≤10% of the measurement for components with a surface concentration >1 mole %. Large uncertainties in the relative elemental sensitivity factors can introduce absolute errors of a factor of 2 or greater. The detection limit is about 0.1 surface mole %, but spectral overlaps between large peaks and small peaks can make it impossible to detect minor components, particularly when more than one chemical state is present for a given element.

8.2   XPS Results

The XPS results for a subset of the paint samples irradiated at The Aerospace Corporation, and appropriate pretest samples, are shown in Table 13. Changes in solar absorptance induced by the exposure are also indicated in the table for the irradiated samples. The concentrations of K, Si, Zn, Ti, S, and O have been calculated on a carbon-free basis to make comparison of the samples before and after irradiation easier. It is thought that the carbon is present primarily due to surface contamination of the coatings from the combined effects of fabrication, atmospheric exposure, handling, and testing. The carbon concentrations on the virgin surfaces ranged from 11 to 22 atom %. This is characteristic of carbonaceous residue on oxide surfaces. Low percentages of carbon in the binder formulation would be masked by surface contamination. XPS depth profiles of two YB-71P samples at WL[15] showed that most of the carbon was removed after 10 s sputtering.

The Aerospace post-test surfaces showed a significant increase in carbon concentration, ranging from 25 to 67 atom %. A carbon concentration of 50 mole % would be measured by XPS for a surface with approximately 15Å of uniform hydrocarbon residue.[16] The increased carbon on the paint surfaces was most likely caused by cracking of adsorbed molecules from residual gases in the test chamber during 40-keV electron and UV irradiation. The vacuum in the test chamber was maintained in the low 10^{-8} torr range during sample exposure. Although the SCEPTRE exposure facility was at somewhat higher pressure[8] (5×10^{-8} to 5×10^{-7} torr) during WL tests, the irradiated thermal control coatings had lower post-test carbon concentrations of 15 to 36 atom %. The lower electron energy, 10 keV, used in the SCEPTRE exposures may have resulted in less cracking of adsorbed species on the surfaces, or their samples may have exhibited less charging from the lower energy electrons employed.

The K:Si atom ratio calculated from XPS data for the pretest white thermal control surfaces was 0.6 ± 0.1 for all of the new formulation batches and two of the old formulation batches analyzed. This is within experimental error of the expected theoretical value of 0.6061. Two virgin samples of the old YB-71 formulation with PS-7 potassium silicate binder, batch P-062, and a batch of unknown designation associated with LDEF (analyzed 10-16-90) had higher K:Si ratios of 1.1 and 1.8, respectively.

Table 13. XPS Results for White Thermal Control Samples

Designation	Surface	Surface Atom % (Normalized Carbon-Free)						C*	K:Si	Δ Solar Absorptance
		K	Si	Zn	Ti	S	O			
YB-71P	Pretest, B-94	9.0	16	1.4	1.3	0.6	71	11	0.6	
T-081/R028	Post-test, B-98	10	14	1.1	0.6	0.9	74	60	0.8	0.238
Kasil 2130	Post-test, B-99	11	13	0.7	0.5	0.5	74	63	0.8	0.235
	1 hour x-rays	13	13	0.9	0.4	0.8	72	63	1.0	
	2.75 hour x-rays	14	16	0.6	0.2	0.6	69	62	0.9	
YB-71P	Pretest X-4	7.4	14	4.5	3.8	nd	71	12	0.5	
S038	Post-test, X-7	11	11	2.3	2.0	nd	73	63	1.0	0.207
Kasil 2130	Post-test, X-8	10	10	2.3	2.3	tr	75	62	1.0	0.221
	Post-test, X-9	12	11	2.2	1.8	0.3	73	59	1.1	0.211
YB-71P	Pretest, A17, Area 1	11	17	1.3	1.3	1.0	68	16	0.6	
S081	Pretest, A17, Area 2	10	16	1.3	1.4	0.9	70	22	0.6	
Kasil 2130	Post-test, A12, Area 1	13	12	0.2	0.7	0.6	73	57	1.1	0.323
	Post-test, A12, Area 2	13	11	1.0	0.5	0.7	73	55	1.1	
	Post-test, A18	13	11	0.7	0.8	0.4	74	48	1.1	0.305
YB-71K	Pretest MM57	12	17	0.1	0.4	1.9	69	12	0.7	
R023	Post-test/darker, MM60	12	16	<0.1	0.3	3.3	69	30	0.8	0.185
Kasil #1	Post-test/darker, MM60	14	18	<0.1	0.2	3.4	64	25	0.8	
	Post-test/dark, MM60	14	17	0.1	0.2	3.0	66	29	0.8	
	Post-test/lighter, MM60	13	15	<0.1	0.4	3.0	69	30	0.9	
	Post-test/lighter, MM60	13	18	0.1	0.3	2.0	67	25	0.7	
YB-71	Post-test, C-001	7.9	12	2.2	1.9	0.3	76	60	0.7	0.129
R123, PS-7	Post-test, C-014	11	9.2	1.5	1.2	0.4	76	67	1.2	0.145
YB-71	Pretest #3	8.8	13	4.3	3.6	0.3	70	12	0.7	
Q051, PS-7	Pretest, #4	9.2	13	4.1	3.5	0.2	70	15	0.7	
	Post-test, #2	12	9.9	1.8	1.8	0.2	75	58	1.2	0.095
YB-71	Pretest, #1	12	10	3.0	3.0	1.9	70	13	1.1	
P062, PS-7	Pretest #3	13	11	2.5	2.6	2.2	69	13	1.2	
	Post-test, #2	16	6.6	1.2	1.3	0.8	74	53	2.5	0.108
YB-71, PS-7	Pretest, 10/16/90	15	8.1	3.6	2.8	nd	71	18	1.8	
Z-93	Post-test, #3	18	3.8	1.7		2.2	75	65	4.6	0.089
PS-7	Post-test, #2	16	6.8	2.9		0.5	74	55	2.3	0.053

* Measured peak areas for all detected elements were corrected by elemental sensitivity factors before normalization to give surface atom %.

nd = not detected, tr = trace

A comparison of XPS results for virgin and irradiated paint surfaces showed that for all batches of materials analyzed, the irradiated surface showed a significant increase in K:Si. The magnitude of the increase varied from 15 to 100% relative to the virgin surface of the batch. The enhancement of K relative to Si at the binder surface can be explained as an effect of the test exposure. The flux of electrons to the paint surfaces will result in a negative charge buildup since the coatings are not electrically conductive. If K^+ ions are generated in the course of the irradiation (e.g., through photoelectron or Auger electron emission), they will tend to migrate toward, and segregate at, the negatively

charged surface. Localized surface heating induced by the irradiation (backside sample temperatures were maintained at 22–27°C by cooling) would increase the mobility of the K^+ ions. Although there were batch-to-batch differences in the K:Si ratio measured after irradiation, no correlation with the change in solar absorptance was observed. This is demonstrated in Figure 14, where the calculated K:Si ratio is plotted as a function of the change in solar absorptance for all the irradiated samples analyzed by XPS.

Figure 8 also provides another striking illustration of the batch-to-batch performance differences in YB-71/P/K. The measurements for multiple samples within each batch are fairly close in solar absorptance, but the different batches are spread along the x-axis. It can be seen that the performance of the YB-71P formulation batches is worse than YB-71K, which is worse than the YB-71 batches. The results for one Z-93 batch was added to the figure for comparison. It had the best solar absorptance performance, but the highest K:Si atom ratio. A test of YB-71P, T081, sample B-99, showed that X-ray exposure for 2.75 h at the conditions of the XPS analyses resulted in a small additional increase in the surface K:Si ratio (from 0.8 to 1.0; see Table 13). Samples were typically exposed to the X-ray beam for 30 min to complete the survey and high-resolution XPS scans.
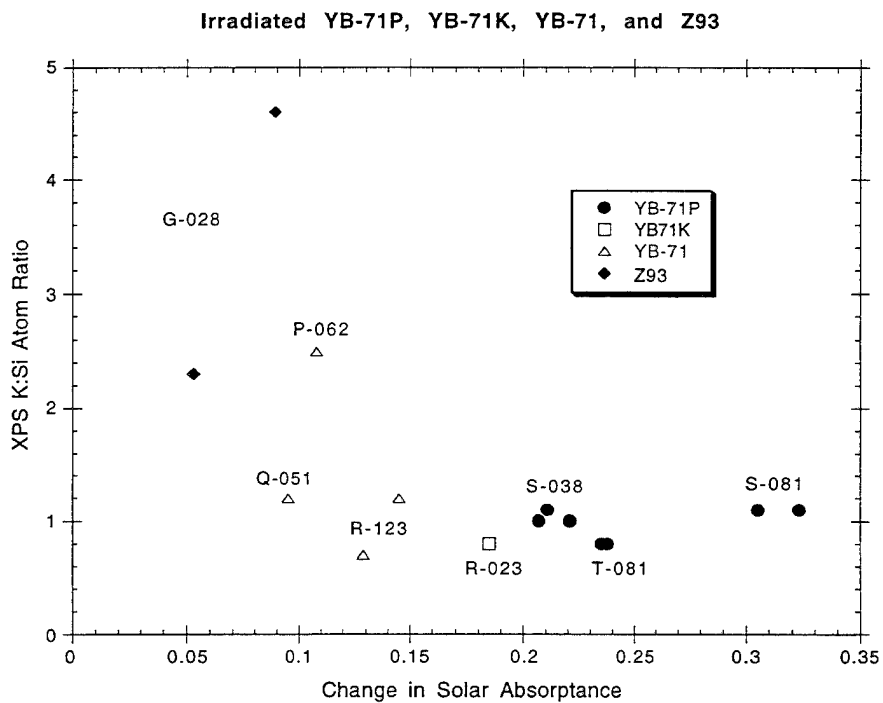
Figure 8.   XPS-determined K:Si atom ratio as a function of the change in
            solar absorptance for white thermal control coatings irradiated at
            The Aerospace Corporation.

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Pretest and post-test XPS data from SCEPTRE-exposed paint samples is compared to Aerospace-exposed samples from the same batch in Table 14. The WL data (indicated in boldface in Table 14) for YB-71P, S038, and YB-71, R123 show an increase in the surface K:Si atom ratio in the post-test analyses relative to the pretest. This is in agreement with the Aerospace data set shown in Table 14. The UDRI data for YB-71P, T081/R028, indicate comparable K:Si ratios pretest and post-test, whereas the Aerospace data for the same batch show an increase on the irradiated surfaces. Thus, there is only one "anomalous" example of K:Si ratio trend in the combined Aerospace/WL data, and no clear understanding has been reached of why the two tests produced such significantly different results for the same batch of coating material.

The WL XPS data for YB-71, R123, sample C-017, shows a K:Si ratio for a visibly darkened area on the surface that was almost a factor of 2 larger than the ratio for an adjacent lighter area on the irradiated material. Two samples of this same YB-71 batch (C-001 and C-014) irradiated at Aerospace had significantly different K:Si surface ratios, although neither was visibly streaked like C-017, and both

Table 14. Comparison of WL and Aerospace XPS Data

| Designation | Batch | Sample No.* | Surface | Surface Atom % | | Atom Ratio |
				S	C	K:Si
YB-71P	T081/R028	B-94	Pretest	0.6	11	0.6
	Kasil 2130	B-98	Post-test	0.9	60	0.8
		B-99	Post-test	0.5	63	0.8
		IITRI 45	**Pretest**	**1.0**	**14**	**2.1**
		IITRI 40	**Post-test**	**nd**	**30**	**2.4**
		IITRI 42	**Post-test**	**nd**	**36**	**2.1**
		IITRI 45	**Post-test**	**1.2**	**18**	**2.1**
		IITRI 45	**Post-test**	**nd**	**15**	**2.0**
YB-71P	S038	X-4	Pretest	nd	12	0.5
	Kasil 2130	X-7	Post-test	nd	63	1.0
		X-8	Post-test	tr	62	1.0
		X-9	Post-test	0.3	59	1.1
		X-1	**Pretest**	**0.6**	**8.7**	**0.6**
		X-5	**Post-test**	**2.0**	**20**	**0.8**
		X-6	**Post-test**	**nd**	**18**	**0.8**
YB-71	R123	C-001	Post-test	0.3	60	0.7
	PS-7	C-014	Post-test	0.4	67	1.2
		C-018	**Pretest**	**nd**	**17**	**0.7**
		C-017	**Post-test/Dark**	**1.1**	**24**	**1.5**
		C-017	**Post-test/Light**	**nd**	**19**	**0.9**
Z-93	PS-7	#2	Post-test	0.5	55	2.3
		#3	Post-test	2.2	65	4.6
		MM11	**Post-test**	**1.4**	**21**	**0.6**

* WL data indicated in boldface.
nd = not detected, tr = trace

had a similar change in solar absorptance. Five different areas on sample MM60, a YB-71K formulation, were analyzed at Aerospace. This particular irradiated sample had a dark-blue discoloration in the center and one side that was noticeably more blue than the other. The XPS data showed no correlation between the visible extent of the discoloration and the measured K:Si ratio, which was 0.8 ± 0.1 for all five areas.

The Z93 samples analyzed by XPS at Aerospace and WL came from different batches. The data for the irradiated samples show a large difference in K:Si ratio between the Aerospace samples (batch G028) and the WL/UDRI samples. Both batches gave very good performance, with small changes in solar absorptance after test exposures. This is another example of apparent lack of correlation between K:Si ratio and coating performance.

The XPS analyses performed at Aerospace represent an average over an area of about 20 mm^2 (the total irradiated area of the samples analyzed was about 500 to 600 mm^2). The XPS analyses at WL covered an analysis area of about 0.5 mm^2 As there appears to be potential for heterogeneity in the surface composition of these coatings, particularly after irradiation, large analysis areas and/or multiple areas of analysis are desirable. It is believed that the WL hypothesis linking poor performance of a paint batch with its surface K:Si atom ratio was based on an insufficient data base.

Table 14 includes the surface concentrations of S and C, as well as the K:Si atom ratio for the listed samples. As mentioned in the text earlier, it is felt that the increase in surface carbon on the irradiated samples is due to the cracking of adsorbed molecules under the UV/electron flux. The higher electron energy used in the Aerospace exposure facility (40 keV) relative to the SCEPTRE facility (10 and 1 keV) could account for the relatively larger increase in carbon observed post-test on the Aerospace samples. Small percentages of organic compounds throughout the binder, such as proprietary additives, processing residues, or contaminants picked up during handling and storage, would not be readily identified by XPS analysis in the presence of typical surface contamination layers. But the oxidation of such organics introduced into the coating formulation with the binder could extract pigment oxygen during irradiation[17] and result in darkening of the paint. Differences in organic components of PS-7 and Kasil 2130 could help explain the change in performance of the new-formulation coatings. If organic contaminants are introduced during the formulation process itself, there could also be significant effects on individual batches of paint. It is suggested that an analytical comparison be made of potential organic components of the PS-7 and Kasil 2130 binder solutions.

The surface concentrations of sulfur (see Tables 13 and 14) varied from <0.1 (not detected) to 3 atom %. A rather wide range of values was measured for different samples within some batches, in both the Aerospace and WL/UDRI XPS analyses. The source of the sulfur in the paints is not well established, although it could be introduced during the production of the potassium silicate solution.[18] Although the surface concentration of sulfur does not appear to correlate with the change in solar absorptance of the coatings, the oxidation of sulfur-containing compounds such as thiols or sulfides could extract pigment oxygen during irradiation.[17] If possible, a better understanding, and control, of sulfur sources in the coatings might be desirable. If sulfur-containing compounds or organics susceptible to oxidation are unavoidable in the paint, the addition of appropriate additives to replenish pigment lattice oxygen might be an alternative approach to improve coating performance.

9. Discussion

9.1 Current Results

The averaged values for all Aerospace test data for the six paints are given in Table 15. Note that there are two entries for S13GPLO-1, one with and one without the data for batch R055.

Table 16 compares the data for Z-93 from WL and Aerospace tests. The numbers are fairly consistent, with only one sample of batch G028 showing significantly higher degradation than the others. This is somewhat surprising in that all the tests used different exposure conditions. The data from both laboratories on YB-71 is given in Table 17. In this case, the data indicates that significant differences exist, presumably due to test conditions. From the data on batch R026, it would appear that the most stressing test was the ZOT test, using 40 keV electrons, and the least stressing was Paint Test 1, which used 10 and 1 keV electrons as did WL tests, but the samples were cooled. However, the data for batch R123 would suggest that WL 2 was a more stressing test than the ZOT test. The data from WL and Aerospace obtained on YB-71P is presented in Table 18. The data is clearly scattered, leading only to the conclusion that the exposure in Paint Test 1 was the least stressing.

Table 15. Average Values for Paint Properties

Paint	Pretest α	Post-test α	Delta α
Z-93	0.12	0.16	0.04
Z-93P	0.11	0.15	0.04
S13GLO-1	0.17	0.28	0.11
S13GPLO-1	0.15	0.34	0.19
- Batch R055	0.16	0.29	0.13
YB-71	0.10	0.20	0.10
YB-71P	0.09	0.31	0.22

Table 16. Comparison of WL and Aerospace Data on Z-93

Test	Batch #	Sample #	Pretest α	Post-test α	Delta α
WL 1	---	---	0.135	0.185	0.050
WL 2	---	---	0.134	0.178	0.044
PT 1	R009	12	---	0.145	0.025
PT 1	R009	5	0.12	0.145	0.025
ZOT Test	G028	2	0.139	0.192	0.053
ZOT Test	G028	3	0.133	0.222	0.089
PT 2	G028	61	0.138	0.174	0.036
PT 2	G028	62	0.134	0.168	0.034
PT 2	R115	A002	0.109	0.145	0.036
PT 2	R115	A046	0.110	0.145	0.035
PT 2	S044	X-32	0.107	0.154	0.047
PT 2	S044	X-39	0.109	0.142	0.033

Table 17. Comparison of WL and Aerospace Data on YB-71

Test	Batch #	Sample #	Pretest α	Post-test α	Delta α
WL 1	R026	---	0.087	0.232	0.145
WL 1	R026	---	0.090	0.220	0.130
WL 2	R123	---	0.097	0.297	0.200
PT 1	R026	01	0.122	0.199	0.077
PT 1	R123	C015	0.090	0.135	0.045
PT 1	R123	C016	---	0.129	0.039
ZOT Test	R123	C001	0.082	0.211	0.129
ZOT Test	R123	C014	0.079	0.224	0.145
ZOT Test	R026	2	0.137	0.312	0.175
ZOT Test	R026	3	0.125	0.319	0.194

Table 18. Comparison of WL and Aerospace Data on YB-71P.

Test	Batch #	Sample #	Pretest α	Post-test α	Delta α
WL 1	R028	---	0.089	0.282	0.193
WL 1	R028	---	0.092	0.363	0.271
WL 2	R028	---	0.106	0.419	0.313
PT 1	R028	02	0.107	0.229	0.122
PT 1	R028	11	---	0.227	0.120
ZOT Test	R028	5	0.102	0.377	0.275
ZOT Test	R028	6	0.107	0.376	0.269
WL 2	S038	---	0.093	0.266	0.173
WL 2	S038	---	0.097	0.233	0.136
PT 1	S038	X-2	0.093	0.177	0.077
ZOT Test	S038	X-7	0.093	0.300	0.207
ZOT Test	S038	X-8	0.088	0.309	0.221
ZOT Test	S038	X-9	0.088	0.299	0.211

9.2   Comparison to Flight Test Data and Other Ground Test Data

The data obtained from this study can be compared to previous flight experiment data generated on the old formulations. There is a significant amount of other ground test data from contractor facilities on the old formulations that is also relevant. NASA/GSFC has performed a 3100 ESH UV test on the new formulations, and this is included in the data summaries below.

9.2.1   Z-93 Flight Test Data

Z-93 was one of the first white paints to be developed and successfully used on spacecraft. It is not surprising therefore, that there is a large amount of data that has been accumulated over the last 30 years on the flight performance of this material in various orbits and missions. On the other hand, Z-93 has not been used significantly on SMC spacecraft. The only recent data available comes from the Air Force Experiment on the Long Duration Exposure Facility (LDEF).[12,19,20,21,22] Strictly speaking, since LDEF was in a low Earth orbit (LEO) this implies that the data should be compared to UV

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and/or UV/AO ground test data and not to exposures involving charged particles. There is LDEF data on Z-93 for both leading-edge (LE) and trailing-edge (TE) experiments. The leading edge of LDEF allowed exposure of the samples to both UV and atomic oxygen, while the trailing edge essentially had only UV exposure. Thus, it is appropriate to compare LE LDEF data to combined UV/AO exposures and to compare the TE data to UV ground test data. Z-93 was also exposed to the space environment on-board Skylab.[23]

The Z-93 flight test data from these flights is summarized in Table 19. It is obvious from the LDEF data that Z-93 is a very stable paint in the LEO environment. TE samples had a delta α of only about 0.02. Different LDEF investigators report somewhat different results for Z-93, possibly due to their different locations on LDEF and due to varying different amounts of contamination. The Skylab data is somewhat unusual in that there appears to have been excessive contamination of some of the samples leading to much higher absorption than anticipated for such short exposures. Z-93 has been flown on other, earlier spacecraft, notably Pegasus II and III,[24] Orbiting Space Observatory III (OSO-III),[25] Mariner IV,[25] and Lunar Orbiter V.[26] Except for the deep-space Mariner IV flight and the Lunar Orbiter V, these spacecraft were LEO satellites of limited durations. Data obtained from these LEO flights all indicated very little or no change for the thermophysical properties of Z-93. The Lunar Orbiter V and Mariner IV flights indicated some substantial degradation attributed to the additional exposure to low-energy protons from the solar wind. However the presence of contamination is also a possible contributor to the apparent degradation of the absorptance/emittance ratio of this material. Z-93 was also used on the Space Electric Rocket Test Satellite (SERT II) and was exposed to the space environment for 6200 h in a polar, sun-synchronous, 1000-km (540 nmi) orbit.[27] This exposure produced a 0.04 delta α for the paint.

Table 19. Flight Data on Z-93

Preflight	Postflight	Delta α	Flight	Exposure Time	Reference
0.14	0.15	0.01	LDEF LE	69 months	12, 19
0.143	0.177	0.034	LDEF LE	69 months	20, 21
0.145	0.161	0.016	LDEF LE	9 months	20, 21
0.149	0.166	0.017	LDEF TE	69 months	20, 21
0.155	0.17	0.015	LDEF TE	9 months	20, 21
---	0.17	---	LDEF LE	69 months	22
---	0.17	---	LDEF TE	69 months	22
---	---	0.077	Skylab SL1/2	35 days	23
0.157	0.252	0.095	Skylab SL1/2	35 days	23
0.154	0.160	0.006	Skylab SL4	74 days	23
---	---	-0.002	Skylab SL4	74 days	23
0.155	0.334	0.179	Skylab SL1/3	131 days	23
---	---	0.174	Skylab SL1/3	131 days	23
---	---	0.002	Pegasus II	2000 h	24
---	---	0.002	Pegasus III	1000 h	24
0.17	---	0.005	OSO-III	1580 h	25
---	---	0.12	Mariner IV	3000 h	25
---	---	0.08	Lunar Orb. V	2000 h	26
0.16	---	0.04	SERT II	6200 h	27

9.2.2 Z-93 Ground Test Data

The ground test data for Z-93 includes a study by TRW[24] that exposed several thermal control materials to UV, electrons, and protons. Z-93 has been exposed to UV and atomic oxygen at NASA/LeRC[29] and at NASA/MSFC.[30] Exposures to UV alone have been performed by NASA/GSFC,[31] Martin Marietta,[32] NASA/MSFC,[4] NASA/Ames,[6i] and MDAC.[6f] There is also a lot of older test data on Z-93 and paints closely resembling Z-93 (ZnO/K_2SiO_3) from the latter 1960's time frame.[6a–6p] Much of the data was generated as companion ground studies to the various flight experiments listed in Table 19. Z-93 was exposed to separate and combined environments by Streed[6i] at NASA/Ames using UV and protons of various energies and various temperatures. Other work at NASA/Ames involved the exposure to UV at high sun intensity by Arvesen.[6e] Reseachers at Hughes exposed Z-93 to a simulated three-year dose of electrons and protons;[33] however, no UV exposure was included in the work. Table 20 summarizes the pertinent ground test data for Z-93, including the results of this work. Exposures that involved atomic oxygen[29,30] have not been included.

Inspection of the data indicates that similar to the flight results from LDEF, the UV/VUV ground tests indicate excellent stability for the Z-93 materials. Values of roughly 0.02–0.04 for delta α are slightly in excess of the flight values for exposures involving roughly two sun intensity levels. The effect of high sun intensity (1–2 vs 25) on the delta α values can be seen as increased degradation (roughly 2×). Comparison of the total solar exposures for the two data sets—11,000 h (LDEF) vs 5000 h (NASA/MSFC)—would indicate that the ground test slightly overpredicts the flight results. The Z-93P sample exposed by NASA/GSFC showed degradation slightly higher than the older Z-93. The

Table 20. Ground Test Data for Z-93/P

Pretest	Posttest	Delta α	Radiation	Intensity	UV Exposure Time	Remarks	Reference
---	---	0.02	UV	2 suns	7067 ESH		6f
0.147	0.203	0.056	UV	25 suns	5900 ESH		6e
0.174	0.202	0.028	UV	1-2 suns	5000 ESH		4
0.14	0.17	0.03	UV/VUV	---	1000 ESH		28
0.145	0.184	0.039	UV	1-2 suns	3100 ESH	Z-93P	27
---	---	0.03	UV/VUV/H$^+$	10 suns (2)	750 ESH (2)		6i
0.19	0.52	0.33	UV/VUV/e$^-$/H$^+$	2-3 suns (1)	1900 ESH (1)		28
0.18	0.25	0.07	e$^-$/H$^+$	(3)	none		33
0.14	0.19	0.05	UV/e$^-$	3.0 suns	3000 ESH	WL	9
0.12	0.16	0.04	UV/e$^-$	2 suns	2300-2600 ESH		This work
0.11	0.15	0.04	UV/e$^-$	2 suns	2300-2600 ESH	Z-93P	This work

(1) TRW exposure involved: 30 KeV protons: 7.3×10^{16} /cm^2, 7 KeV electrons: 7.5×10^{16} /cm^2, and 800 KeV electrons: 4.1×10^{16} /cm^2, 1900 ESH NUV, 1651 ESH VUV.

(2) NASA/Ames exposure involved: 10 KeV protons: 2×10^{15} /cm^2, 750 hr. at 10 suns intensity.

(3) Hughes exposure involved: 50 KeV electrons: 9.0×10^{13} /cm^2, 100 KeV electrons: 1.4×10^{15} /cm^2, 140 KeV protons: 8.3×10^{13} /cm^2.

values of 0.04 obtained in this work compare well with the data from flight and UV/VUV alone. However, dramatically different results were obtained in the TRW study attempting to simulate a 10-year GEO exposure using UV, electrons, and protons. Their delta α of 0.33 is an order of magnitude higher than other data. Similar work at Hughes[33] using different charged particle energies resulted in a delta α of only 0.07. However, the Hughes study did not include UV in the exposure conditions. Unfortunately, for this paint, there is no GEO data for comparison.

9.2.3   S13GLO Flight Test Data

Many investigators[12,19,20,21,22,34,35] had samples of S13GLO on LDEF; hence, there is a substantial amount of data on the response of this material to the LDEF environment. As before with Z-93, there is both leading- and trailing-edge exposure data for this paint. The trailing-edge data is more relevant. Other flight test data comes from the Navstar Global Positioning Satellite (GPS) program, which had samples of S13GLO on a flight calorimeter to assess its degradation in the GPS orbital environment.[36,37] The GPS orbit is roughly one-half that of a GEO orbit, being approximately 11,500 nmi and inclined at 55°. Substantial doses of electrons and protons are seen by spacecraft surface materials in this orbit, comparable to that received in a GEO orbit. The flight data on S13GLO is given in Table 21. Note that all the flight data is on S13GLO, which used the older RTV 602 silicone binder, not S13GLO-1, which contains the newer SWS-884 silicone material. Since the dominant mechanism of degradation of this material may be darkening of the silicone binder, direct comparisons of the flight data with more current S13GLO-1 may be unwarranted. S13 and S13G, both earlier versions of S13GLO, were flown on various spacecraft as was Z-93. Since these versions of the paint are not representative of current or even recent materials, the data are not included in this report.

The flight data indicates that S13GLO is not a space-stable white paint. LDEF TE samples exposed to UV alone showed large increases in delta α. Samples exposed on the LE displayed less degradation due to the scrubbing/cleaning effects of atomic oxygen. The GPS data also indicates a large

Table 21. LDEF/Navstar GPS Data on S13GLO

Preflight	Postflight	Delta α	Location	Exposure Time (Months)	Reference
0.18	0.37	0.19	LDEF LE	69	12, 19
0.148	0.266	0.118	LDEF LE	69	20, 21
0.150	0.475	0.325	LDEF TE	69	20, 21
0.158	0.233	0.075	LDEF LE	9	20, 21
0.154	0.238	0.084	LDEF TE	9	20, 21
0.147	0.232	0.085	LDEF LE	69	34
0.147	0.466	0.319	LDEF TE	69	34
---	0.18	---	LDEF LE	69	22
---	0.28	---	LDEF TE	69	22
0.158	0.182	0.024	LDEF LE	10	35
0.163	0.206	0.043	LDEF LE	69	35
0.18	0.45	0.27	GPS	24	36, 37

increase in absorptance after two years; however, a significant portion of this degradation may be attributable to contamination since second-surface mirrors also flown on the calorimeter indicated substantial degradation.

Data on on S13GLO from the Navstar/GPS flights are presented in Graph 81 in the Appendix.[31, 32]

9.2.4   S13GLO-1 Ground Test Data

The pertinent ground test data for S13GLO-1 is summarized in Table 22. A large amount of work was performed in the 1960's on the predecessor to S13GLO, S13G.[6] S13G did not use a vacuum-stripped silicone in its formulation and, hence, was prone to significant outgassing. The result of such outgassing was usually excessive degradation of the optical properties of the sample from contamination during the test exposure. Since these materials are not representative of current S13GLO-1, the data are not included here. The results of this work are also included for comparison.

The ground test data seems to underpredict the results of most of the LDEF TE exposures and also the GPS data. The exceptions to this invlove again the TRW study, which gives a fairly large overprediction, and the LDEF data from Linton,[22] who observed significantly less degradation than other LDEF investigators, and more in line with the posttest values obtained from ground UV exposures. In any case, S13GLO-1 is clearly not as stable as Z-93.

Table 22. Ground Test Data for S13GLO-1/P

Pretest	Posttest	Delta α	Radiation	Dose/Rate	UV Exposure Time	Remarks	Reference
0.184	0.245	0.061	UV	1-2 suns	5000ESH	S13GLO	4
0.208	0.233	0.025	UV/e$^-$	2 suns	700 ESH	S13GLO-1	5
0.17	0.21	0.04	UV/VUV	---	1000 ESH	S13GLO-1	32
0.193	0.229	0.036	UV	1-2 suns	3100 ESH	S13GPLO-1	31
0.26	0.71	0.45	UV/VUV/e$^-$/H$^+$	2-3 suns (1)	2290 ESH (1)	S13GLO-1	28
0.17	0.28	0.11	UV/e$^-$	2 suns	2300-2600 ESH	S13GLO-1	This work
0.15	0.34	0.19	UV/e$^-$	2 suns	2300-2600 ESH	S13GPLO-1	This work

(1)   TRW exposure involved: 30 KeV protons: 6.6×10^{16} /cm^2, 7 KeV electrons: 1.1×10^{17} /cm^2, 2290 ESH NUV, 1073 ESH VUV.

9.2.5   YB-71 Flight Test Data

The flight test data for YB-71 is shown in Table 23. There is both LEO and GEO flight data for this material. Many investigators had samples of YB-71 on LDEF that were exposed for various durations. YB-71 was flown on calorimeters on three separate DSP spacecraft, hence the large number of entries in Table 23. Some samples were on aluminum substrates, while others were on magnesium AZ31B substrates.[31,32] Samples flown on LDEF and DSP were certainly early production batches and probably do not reflect modifications in paint processing since then.

Table 23. LDEF/DSP Flight Data on YB-71

Preflight	Postflight	Delta α	Location	Exposure Time (Months)	Reference
0.093	0.145	0.052	LDEF LE	69	20, 21
0.087	0.162	0.075	LDEF TE	69	20, 21
0.090	0.153	0.063	LDEF LE	9	20, 21
0.089	0.150	0.061	LDEF TE	9	20, 21
0.13	0.15	0.02	LDEF LE	69	19
0.10	0.11	0.01	LDEF LE	69	19
0.130	0.182	0.052	LDEF LE	69	34
0.130	0.182	0.052	LDEF TE	69	34
0.121	0.123	0.002	LDEF LE	10	35
0.128	0.125	-0.003	LDEF LE	69	35
---	0.17	---	LDEF LE	69	22
---	0.18	---	LDEF TE	69	22
0.202	0.336	0.134	DSP	29	31, 32
0.189	0.351	0.162	DSP	29	31, 32
0.193	0.373	0.180	DSP	55	31, 32
0.180	0.311	0.131	DSP	35	31, 32
0.222	0.372	0.150	DSP	35	31, 32
0.183	0.270	0.083	DSP	26	31, 32
0.202	0.385	0.183	DSP	60	31, 32

The LDEF TE data would indicate that YB-71 is fairly stable to the LEO environment, undergoing a small increase in solar absorptance of about 0.05–0.08. This is in dramatic contrast to the degradation observed on the GEO DSP flights where much larger increases of 0.13–0.18 are seen. Mirrors flown on these flights showed very little degradation, indicating that this increase in absorptance of the paint is due to the GEO radiation environment.

Data on YB-71 from the DSP flight calorimeters are presented in Graph 81 in the Appendix.[31, 32]

9.2.6   YB-71 Ground Test Data

The available ground test data for YB-71 is presented in Table 24. During the development of this material, several samples were included in a 5000-h UV test run at NASA/MSFC.[4] YB-71 was also included in the TRW study.[24] Data from Martin Marietta[32] and NASA/GSFC[31] is also included along with the results of this work.

Table 24. Ground Test Data for YB-71/P

Pretest	Posttest	Delta α	Radiation	Dose/Rate	UV Exposure Time	Remarks	Reference
0.149	0.166	0.017	UV	---	5000 ESH		4
0.131	0.151	0.020	UV	---	5000 ESH		4
0.155	0.166	0.011	UV	---	5000 ESH		4
0.174	0.193	0.019	UV	---	5000 ESH		4
0.122	0.145	0.023	UV	---	5000 ESH		4
0.13	0.19	0.06	UV/VUV	---	1000 ESH		32
0.106	0.267	0.161	UV	1-2 suns	3100 ESH	YB-71P	31
0.15	0.65	0.50	UV/VUV/e$^-$/H$^+$	2-3 suns (1)	2290 ESH (1)		28
0.10	0.20	0.10	UV/e$^-$	2 suns	2300-2600 ESH		This work
0.09	0.31	0.22	UV/e$^-$	2 suns	2300-2600 ESH	YB-71P	This work

(1)   TRW exposure involved: 30 KeV protons: 6.6×10^{16} /cm^2, 7 KeV electrons: 1.1×10^{17} /cm^2, 2290 ESH NUV, 1073 ESH VUV.

The assembled ground data indicates significant variability in the testing results on YB-71. Early data from the development program indicated that the material was very stable to UV with delta α in the range of 0.01–0.02. However, the Martin Marietta test indicated a significantly higher degradation of about 0.06. The results from NASA/GSFC on YB-71P are substantially higher, with a value of 0.16 for delta α. The data from this work and WL indicate that there is a factor of 2 increase in the degradation of YB-71P vs YB-71, and that these values are similar to the values obtained from DSP flight data. As with the other two paints, the data from the TRW study grossly overpredicts the degradation of this material, with a delta α of 0.5.

10. Conclusions

Exposure of the three IITRI white thermal control coatings to UV and electrons in vacuum in multiple tests has produced data on the performance of the newly reformulated versions. The data supports the conclusion that the new version of Z-93, known as Z-93P, performs as well as the older material. While some samples of Z-93P displayed a tendency to crack or delaminate during vacuum exposure, the phenomenon appears to be sporadic. Small changes in water concentration and/or surface preparation could be the cause of this. Degradation of Z-93 and Z-93P occurs, resulting in an increased absorption in the visible and UV regions from roughly 400 to 800 nm. The specimens sometimes appear slightly yellowish after testing. Absorption bands are sometimes observed centered at around 500 nm, and are hypothesized to be due to reduction of Zn^{+2}. Tests on stored samples of Z-93 from 1981 production suggest that newly produced material exhibits slightly less degradation. This may be due to aging effects in the Z-93 or to unknown improvements in paint manufacture. The average value for delta α in this material is 0.04.

For S13GLO-1 and its new formulation S13GPLO-1, similar results have been obtained. However, anomalous results were obtained for every sample of one batch (R055) of S13GPLO-1. The material exhibited dark streaks and lines, perhaps due to charging and arcing. The samples had increased absorption throughout the spectrum and were significantly darker than all other specimens. Generally, S13GLO-1 and S13GPLO-1 degrade, producing absorption in the visible from 400 to 700 nm, with some loss in transmission in the near IR. The samples appear light tan or dark brown depending on the degree of degradation. With the exception of the one batch of S13GPLO-1, the two formulations of the paint perform comparably. The average delta α for S13GLO-1 is 0.11 and 0.13 for S13GPLO-1. The R055 batch had a delta α of 0.30.

Different results were obtained for YB-71 and its new formulation, YB-71P. Extensive testing of several batches and samples of these materials repeatedly indicated that YB-71P exhibited markedly more severe degradation than YB-71. While there are batch-to-batch differences, in every case the YB-71P degraded more than the YB-71, demonstrating that this phenomenon is not a batch issue but rather is due to some interaction between the pigment and the new binder material Kasil 2130. Attempts at identifying a component in this material that could be responsible for this reaction were inconclusive. The degradation of YB-71 is manifested by a graying of the paint sample. The absorption spectrum shows bands at roughly 500 nm and a flat absorption from between 700 and 900 nm. YB-71P, on the other hand, displays a prominent absorption peak centered at 950 nm, which is ascribed to Ti^{+3} produced by reduction of Ti^{+4} in the pigment. It is believed that an unidentified component in the Kasil 2130 promotes the reduction of Ti^{+4}.

Testing of various batches and samples of YB-71 also indicated that older production material such as was manufactured in 1981 exhibited markedly less degradation than material produced in the 1992 time frame. Moreover, batch R026 performed particularly poorly showing as much degradation as some batches of YB-71P. While this material and YB-71P batch R028 used the identical pigment, their response to UV and electrons is significantly different, producing different absorption spectra. This data and the analysis of representative pigment samples indicated that the degradation of these two materials does not appear to be characteristic of this pigment batch. While IITRI paint materials

use pigment blends that have widely varying manufacture dates, it is clear that YB-71 processed in the 1992 time frame exhibits inferior performance relative to older YB-71 materials. The reasons for this are not clear but may reflect subtle processing changes at IITRI. Storage of paint samples at IITRI, as well as potential aging effects on the YB-71 paints, do not appear to affect the performance of the paint in radiation exposure testing.

The testing methodology used in this study has involved posttest reflectance measurements performed in air after venting the test chamber with dry nitrogen. This has worked quite well and produced no visible changes to the samples. The samples retained the substantial radiation damage that was produced during the exposure, and the posttest measurements of this damage correlate fairly well to measurements made by WL/UDRI in vacuum. Similar results were also obtained by WL/UDRI where they observed very small changes in sample reflectance after venting with nitrogen. Exposure to air slowly bleached away a major fraction of the damage after a few days.[9] Significant differences between Aerospace and WL/UDRI results were obtained when the sample temperatures were different or when the electron energies were changed. Generally, higher temperatures produced more damage, primarily in YB-71/P, and the higher 40-keV electrons produced more damage in all the materials tested. Thus, it is recommended that materials be tested at temperatures similar to their intended use temperatures and that energies appropriate to those encountered on orbit be used to simulate charged-particle doses. Analytical modeling of the on-orbit dose depth profile in the material is recommended. From this data, appropriate charged-particle energies can be determined to reasonably approximate the dose in the material as a function of thickness to a reasonable depth, such as 3.0 mil. An elaborate test on these paint materials using UV, high- and low-energy electrons, and high-energy protons has been designed using this methodology, and tentatively will be run cooperatively with NASA/MSFC using their facilities.[8]

Comparison of the data produced in this study and at WL with literature data from flight and ground experiments has indicated significant differences among the results of the various experiments. For Z-93, the majority of the flight and ground data indicates that this material is reasonably stable; values of 0.02–0.05 for delta α are seen for experiments where contamination was not a significant concern. Data for Z-93P are consistent with these results. The exceptions to this low degradation are the lunar and deep space flights where larger degradation was observed in the range of 0.08–0.12. This has been attributed to solar wind exposure. A study by TRW gave an anomalously high value of 0.33 for delta α in this material, suggesting a flaw in their testing methodology or a mishap in their experiment. The situation for S13GLO-1 is not as clear-cut as for Z-93. LDEF data for trailing-edge specimens indicated a substantial degradation of 0.32–0.33 for this material. GPS data indicate a lesser value of 0.27, even with the additional electron and proton fluxes in this orbit. This value is for a two-year exposure as compared to a near six-year LDEF exposure. However, the presence of contamination on the GPS flight samples adds significantly to the degradation, making these numbers difficult to correlate. On the other hand, the ground data for UV exposures significantly underpredict the LDEF data with values of 0.03–0.06. UV/electron exposures also underpredict the data with values of 0.11–0.19. The value of 0.45 from the TRW work, as before, overpredicts the flight data, although it is not as severe as the case for Z-93. The YB-71 data from LDEF indicate modest degradation for this material in the range of 0.05–0.08 delta α for TE samples. The ground UV data vary from 0.01 to 0.06 for this material, and a value of 0.16 was reported for YB-71P. The DSP flight data give values of 0.13–0.18 for the material in a GEO orbit, significantly more than the LDEF data, as expected. The ground UV/electron data from this study and WL are similar to the DSP flight values,

being in the range of 0.10 to 0.22. Substantial differences between the YB-71 and the YB-71P have been observed in both studies. The TRW test with a value of 0.50 for delta α is again far in excess of the flight and other ground test data.

With respect to testing requirements, this study has indicated that there is enough variability in paint performance that it becomes imperative that every batch be tested for space stability. Relying on average numbers is risky and could prove troublesome for spacecraft designed with small margins in their thermal control subsystems. Moreover, it is also apparent that pretest properties are also batch dependent and, therefore, need to be measured. Since testing methods vary, so will the posttest values and, therefore, also the delta α values. It is highly desirable to perform a flight experiment to obtain a better measure of delta α for these current materials. Correlation of such data with ground test data similar to that produced in this study could then be used to generate a simpler, yet reliable, test program to allow screening of paint batches.

A comparison of XPS results for virgin and irradiated paint surfaces showed that the UV/electron irradiation of white thermal control coatings with potassium silicate binder caused an increase in the surface K:Si atom ratio. This effect can be explained by the migration of K^+ ions to the negatively charged test sample surface, aided by localized surface heating. Although there were batch-to-batch differences in the K:Si ratio measured after irradiation, no correlation with the change in solar absorptance was observed. Overall, there was good agreement between XPS results at The Aerospace Corporation and WL/UDRI. As there appears to be potential for heterogeneity in the surface composition of these coatings, particularly after irradiation, large analysis areas and/or multiple areas of analysis are desirable. The oxidation of small concentrations of organics or sulfur-containing compounds could extract pigment oxygen during irradiation. An analytical comparison of organic components of PS-7 and Kasil 2130 is suggested.

In summary, use of the new coating Z-93P as a replacement for Z-93 is recommended based on all of the test data. S13GPLO-1 appears to be an appropriate replacement for S13GLO-1; however, the issue of batch anomalies needs to be further investigated before a blanket approval is given. For YB-71, not only do newer batches of this material perform unsatisfactorily, the replacement of Kasil 2130 as the binder material in this paint yields a material that is sensitive to radiation damage. YB-71P is not recommended for use on spacecraft. More work is needed to address this problem. However, substitution of the apparently more stable (and cheaper) Z-93P for YB-71P in spacecraft applications should be investigated.

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Appendix—Test Data
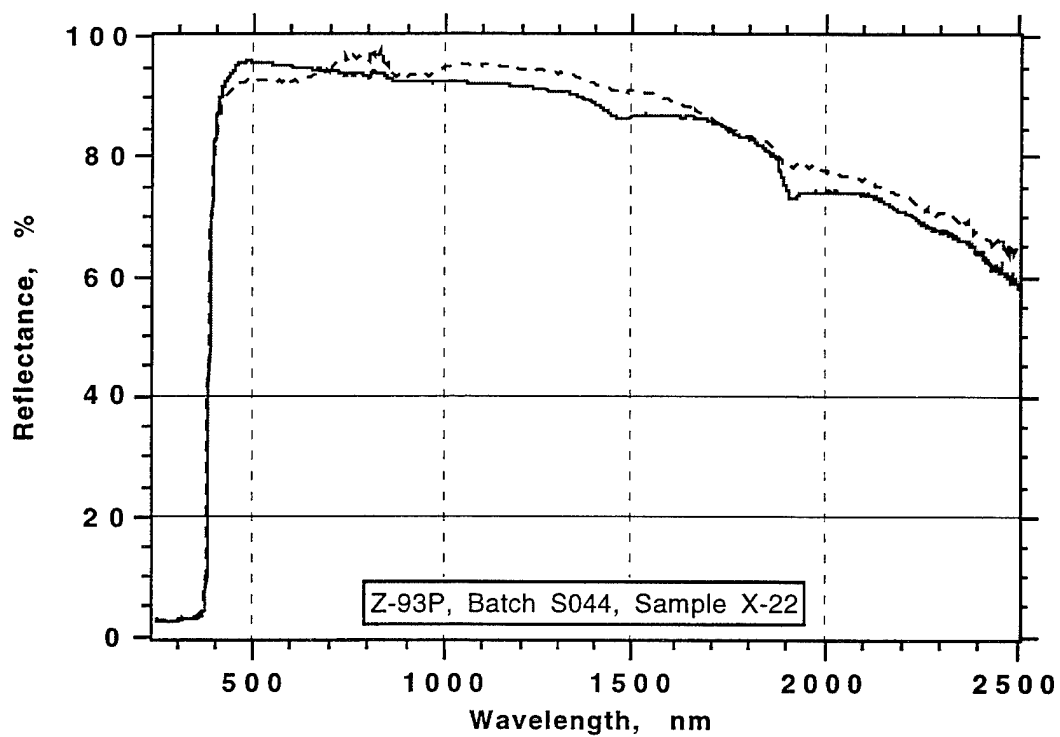
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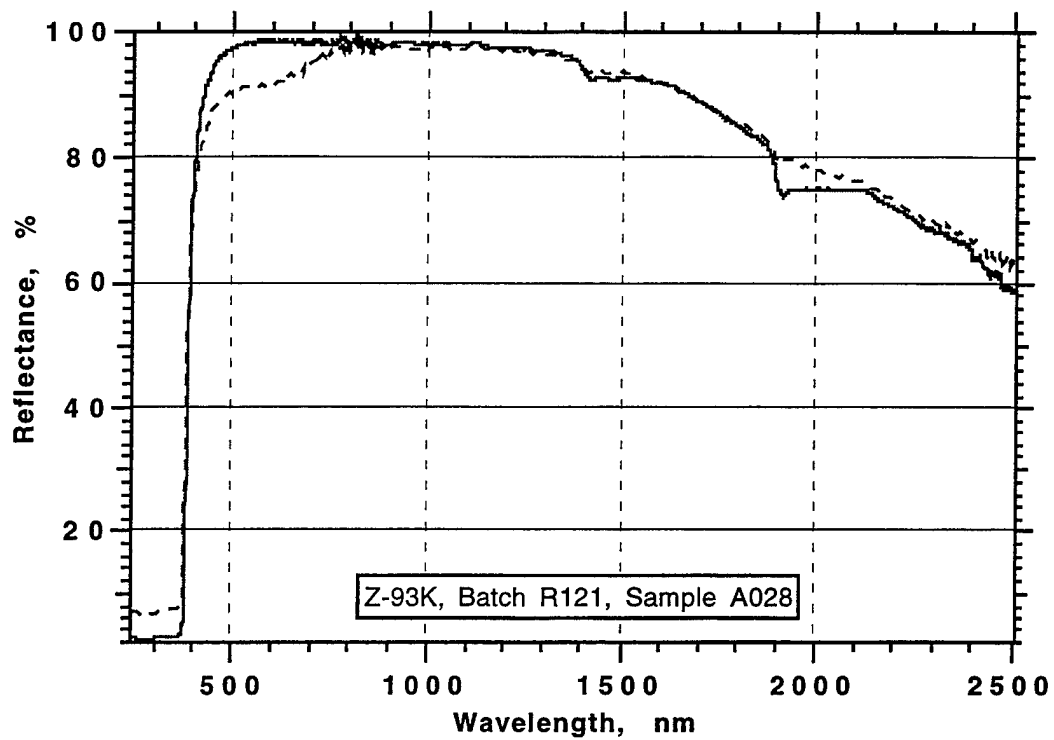

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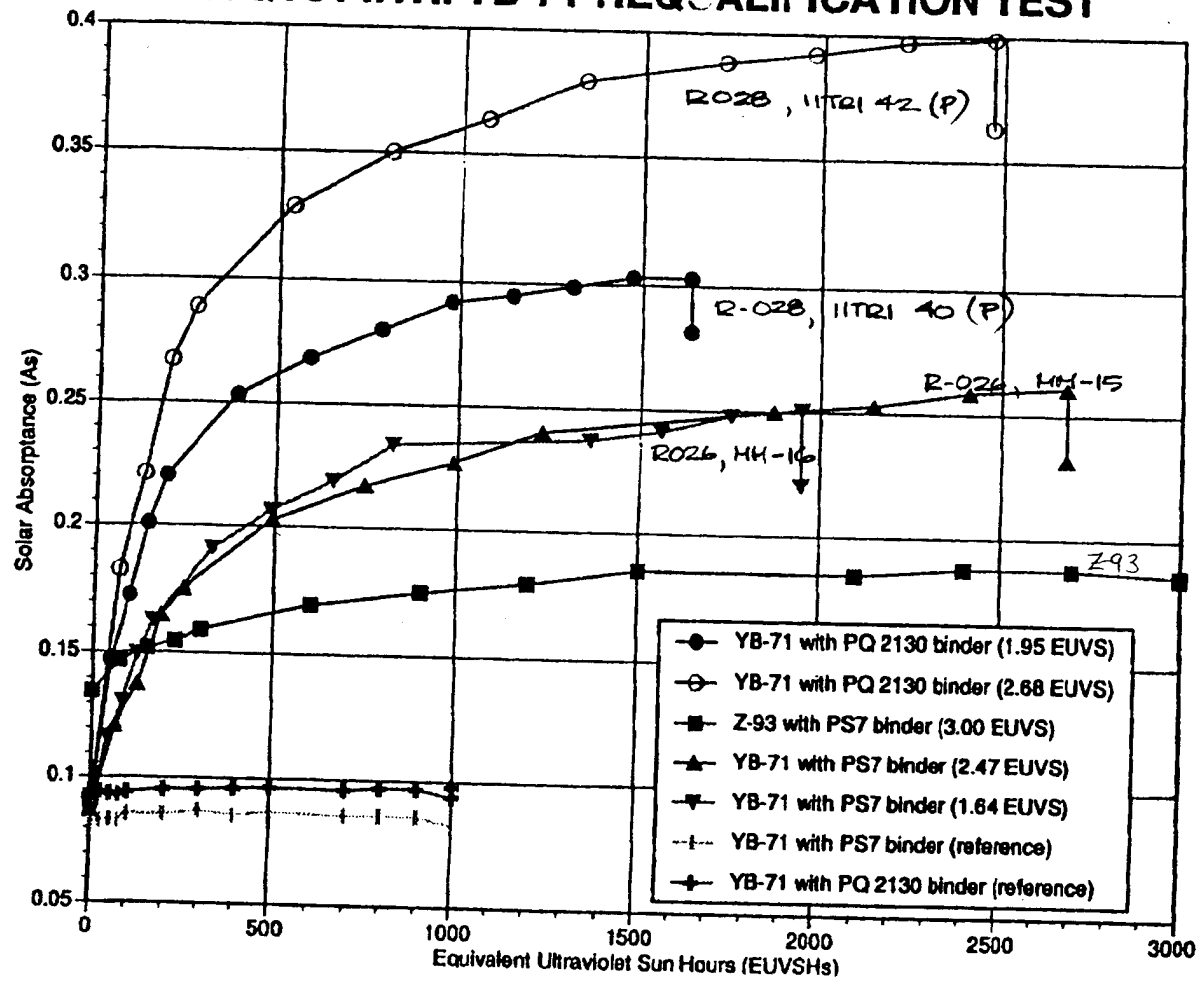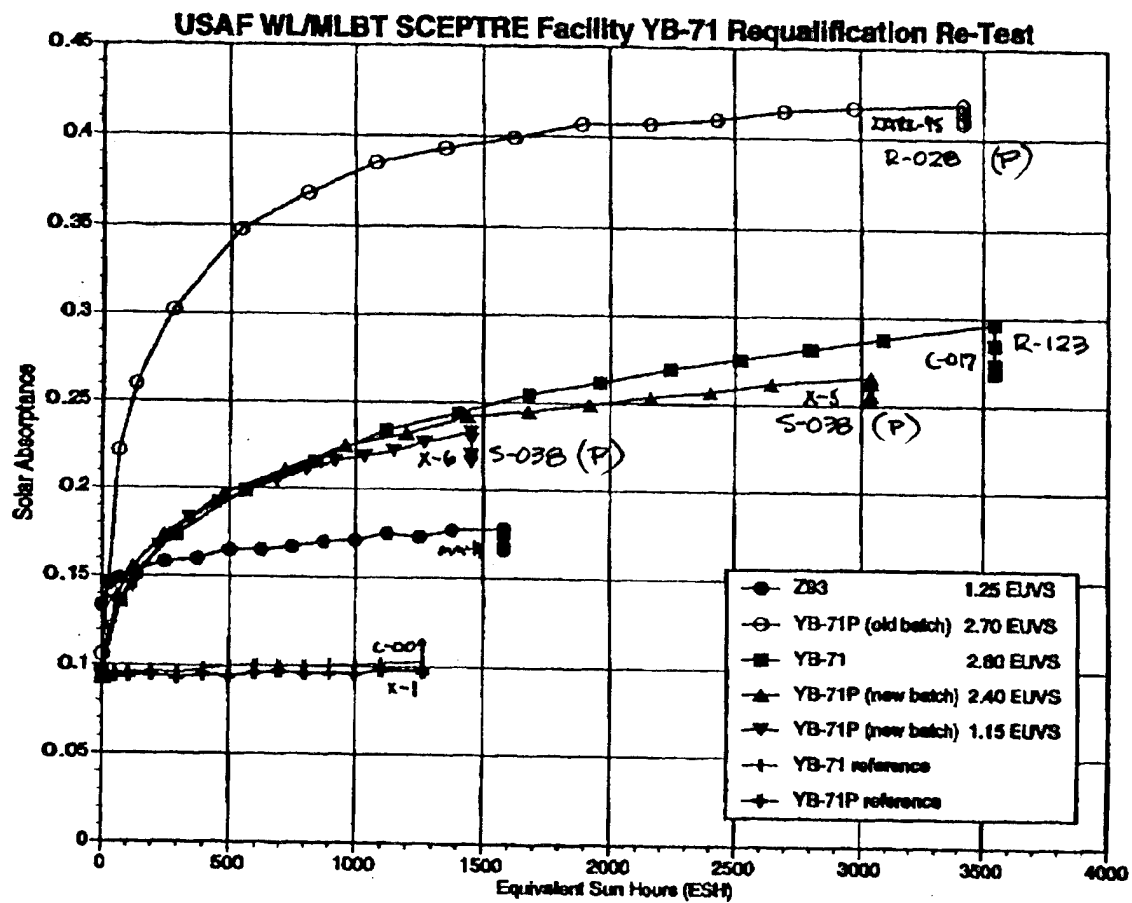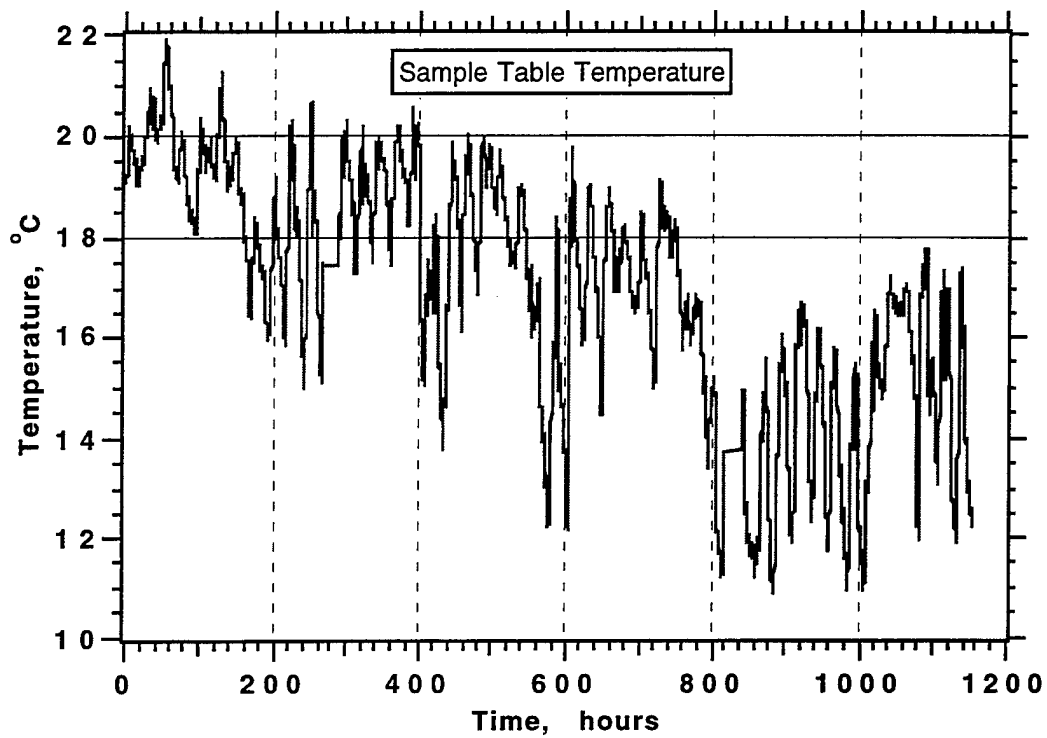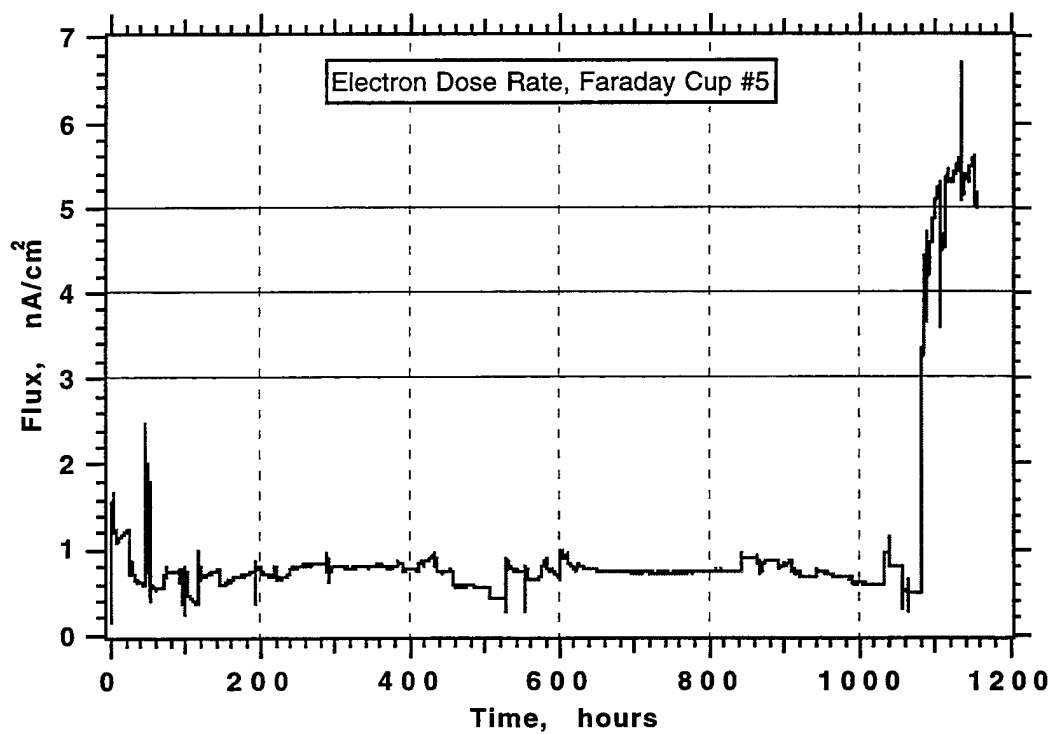
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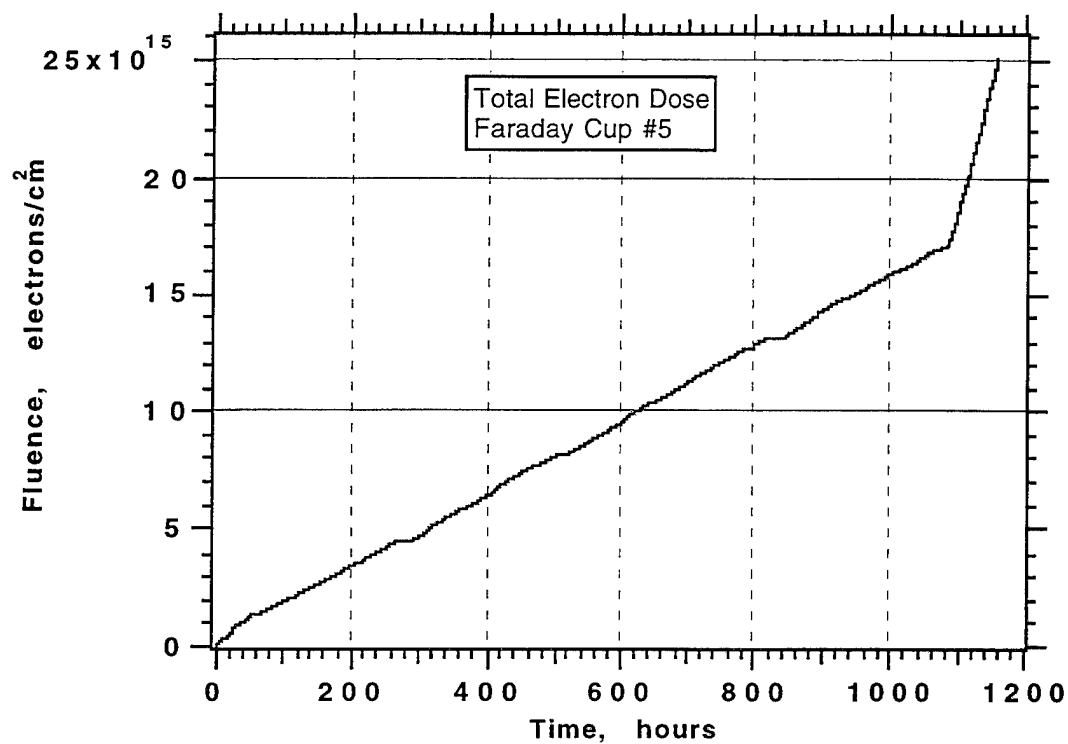
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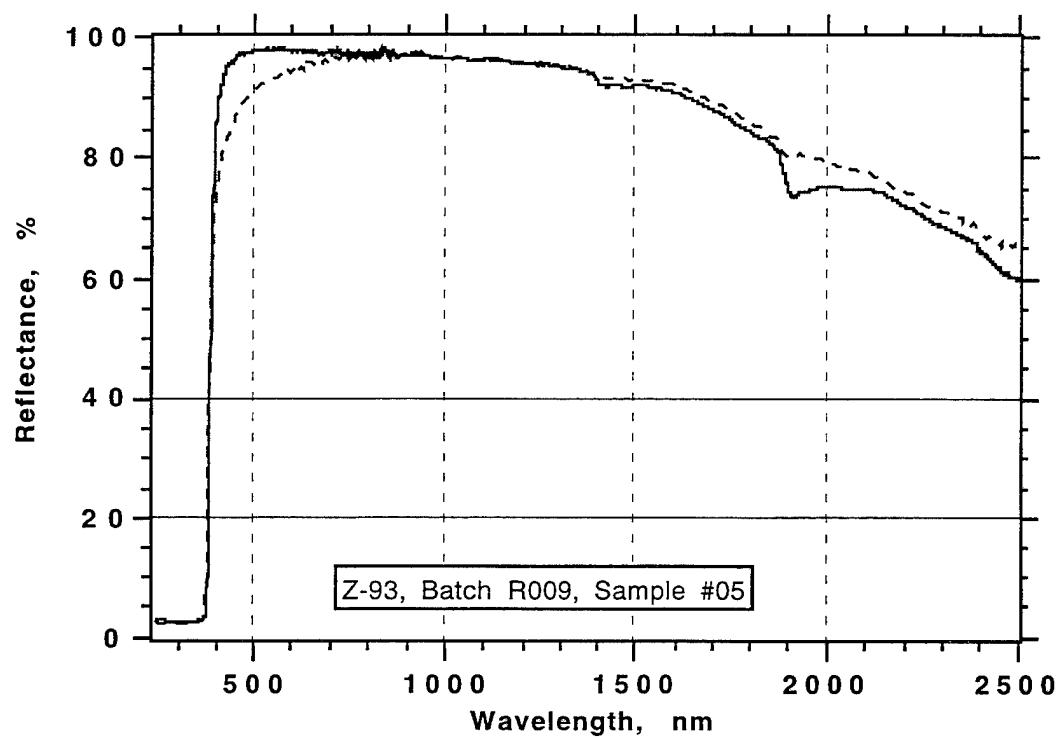
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Graph 7.

Graph 8.

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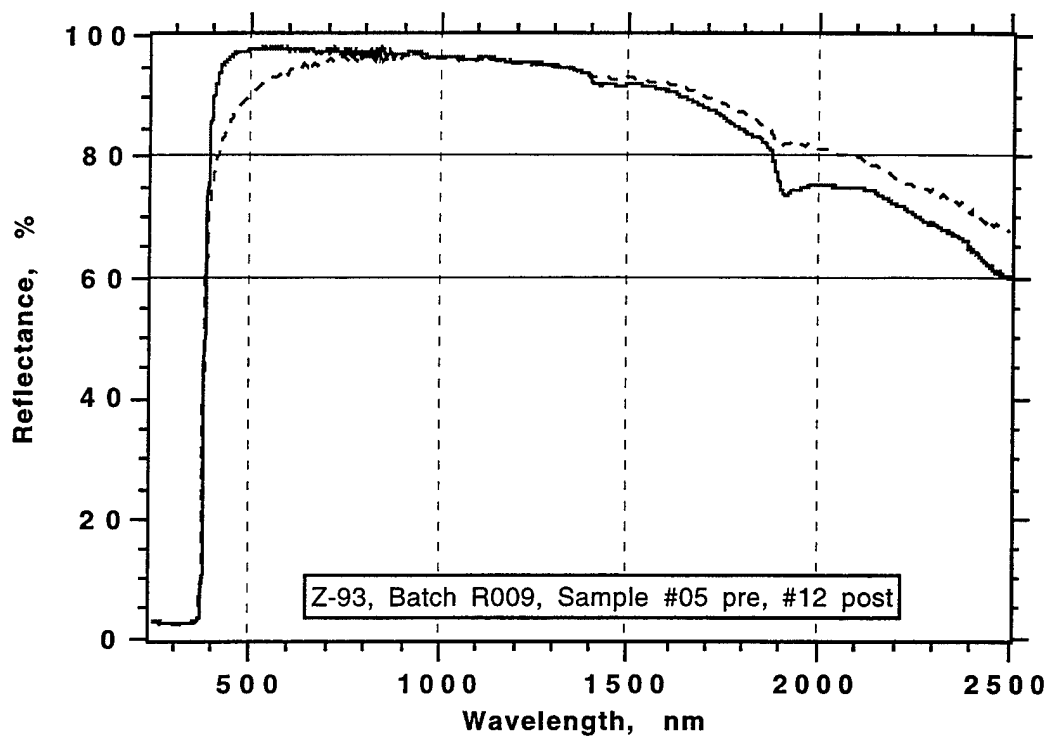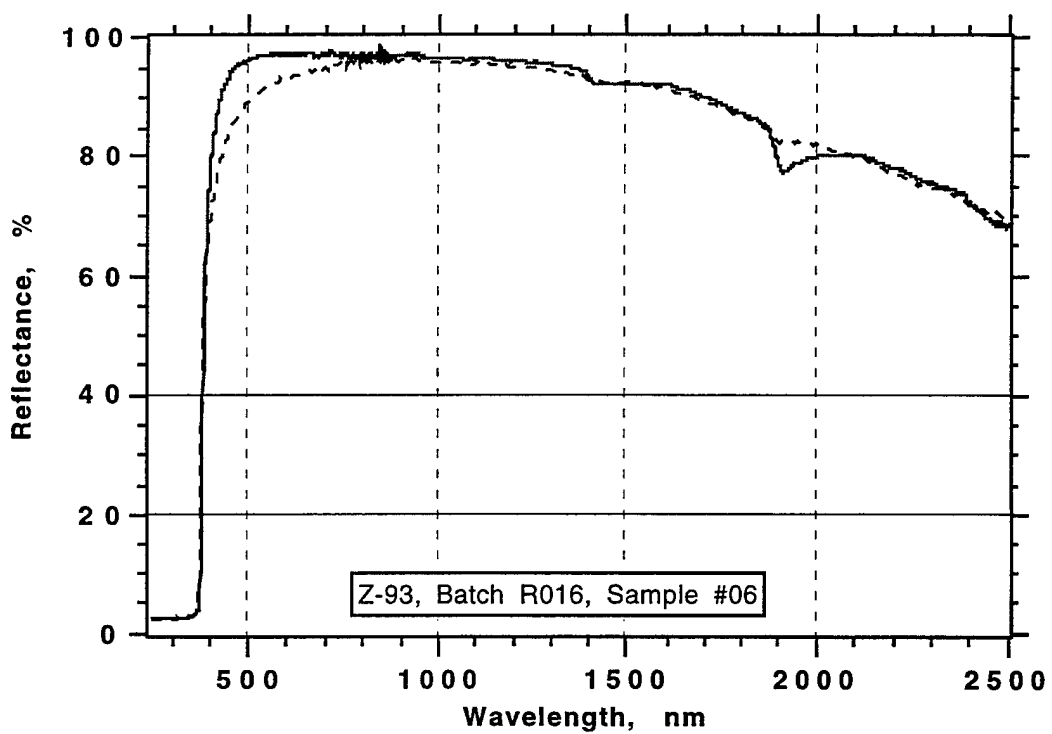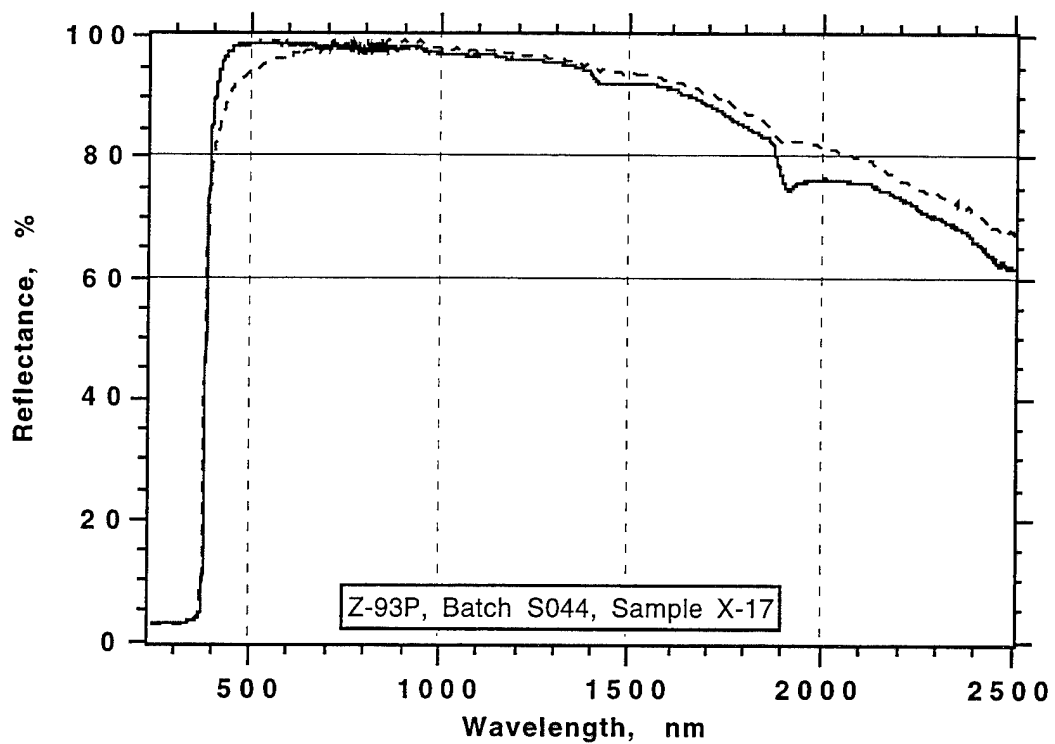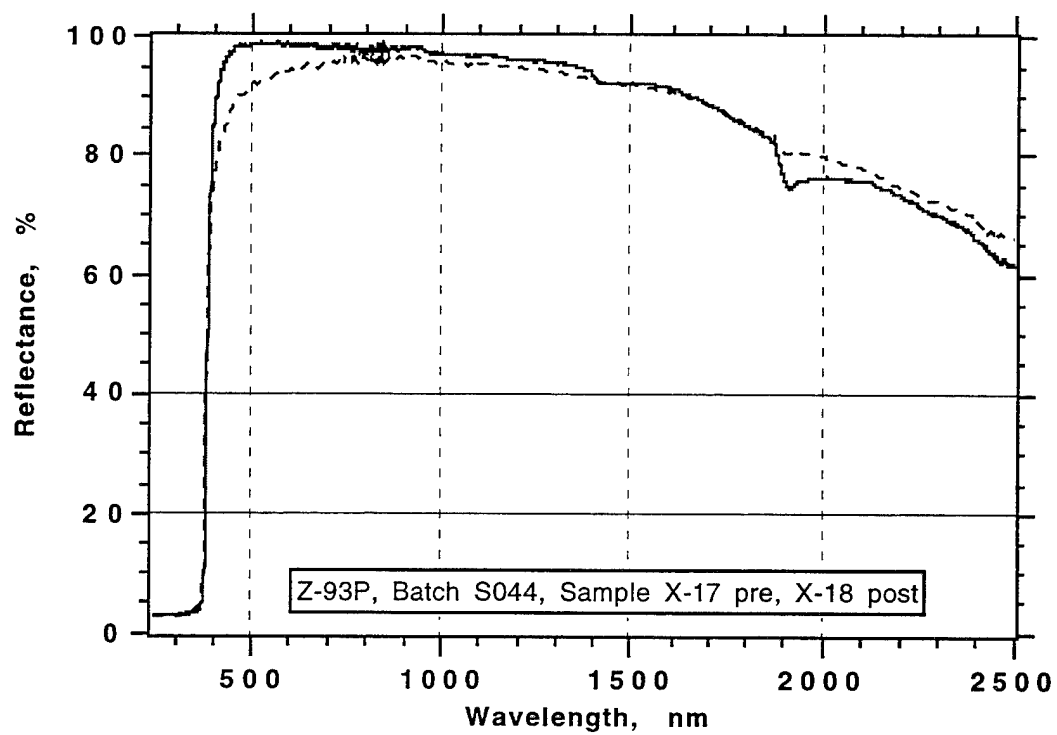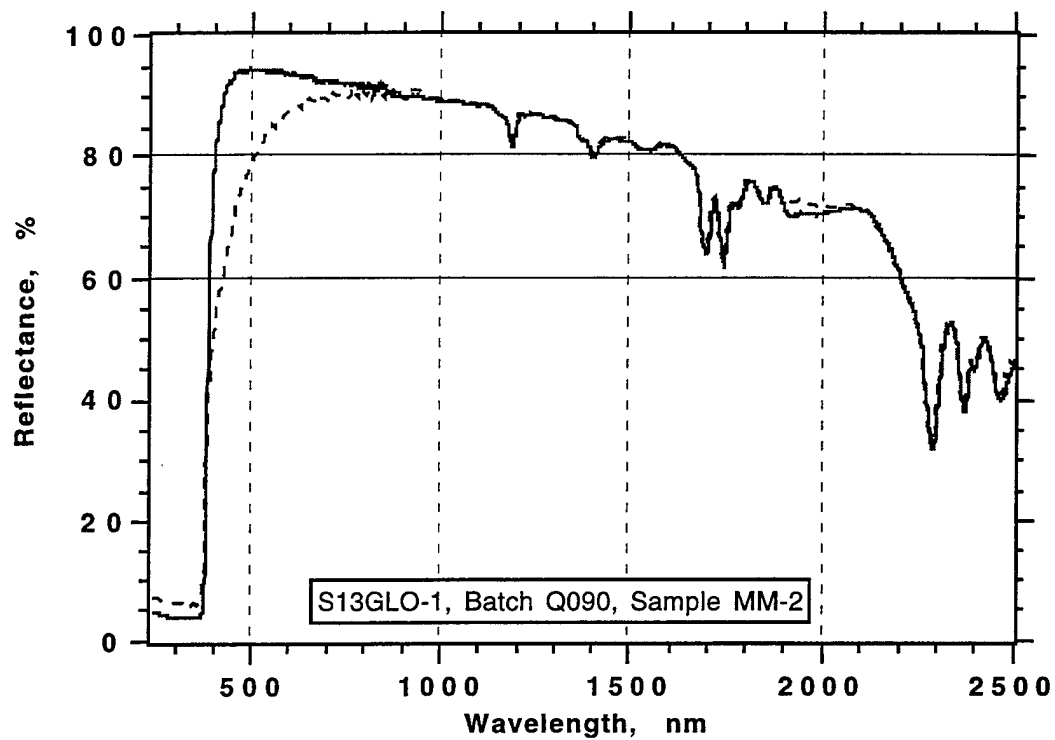
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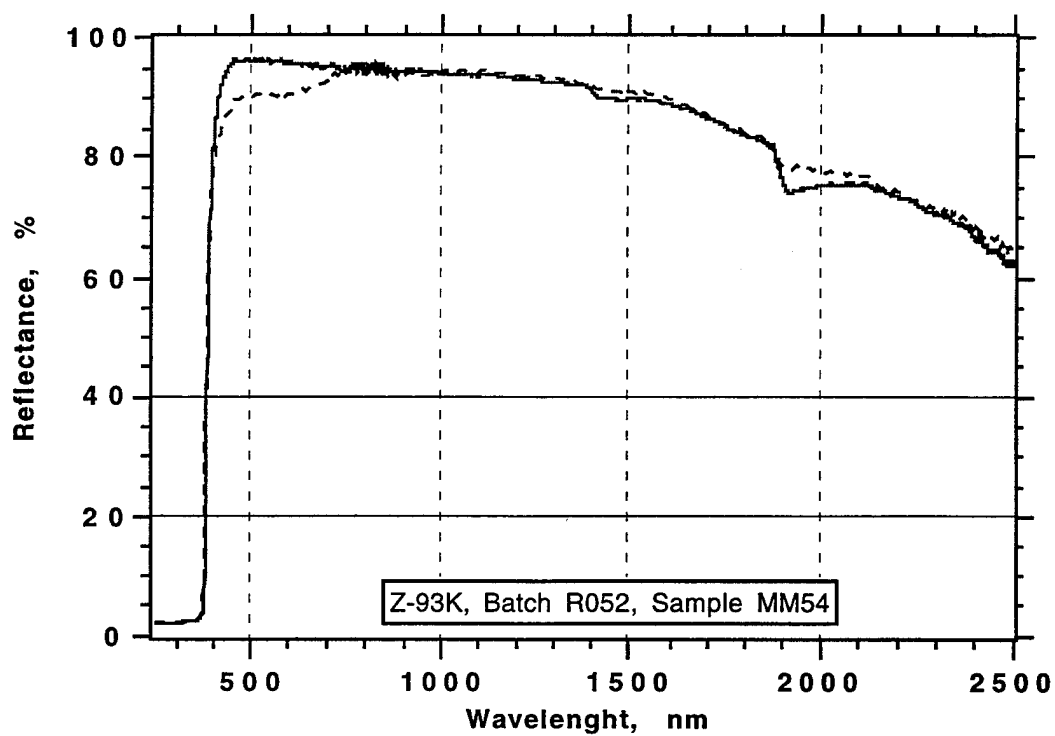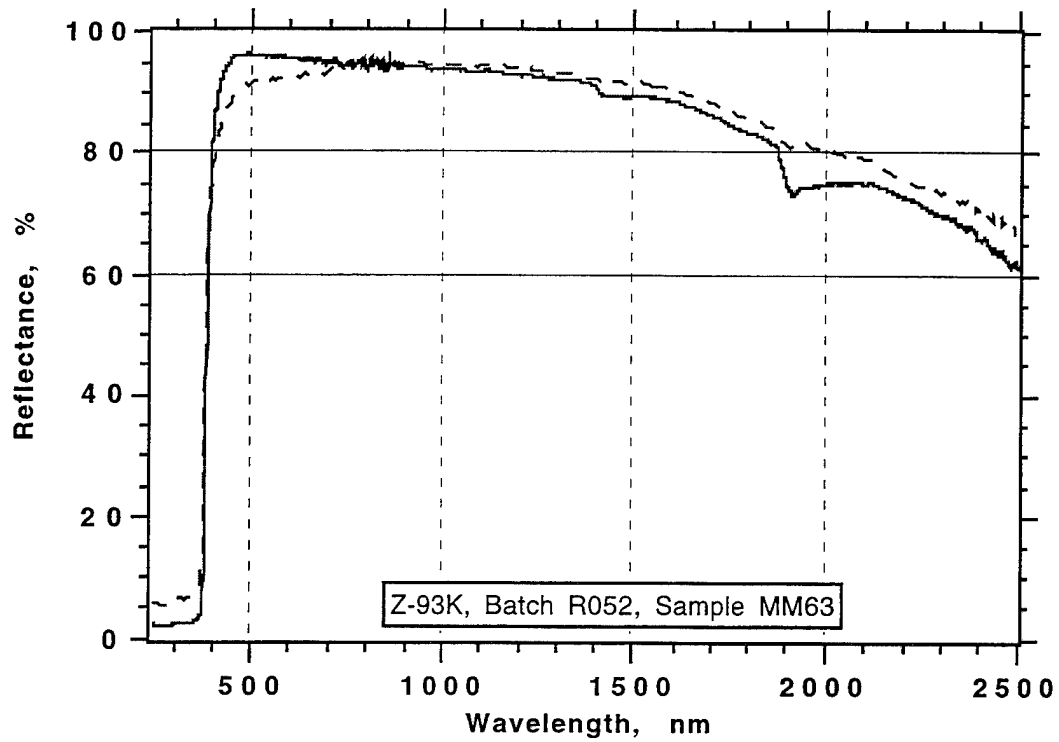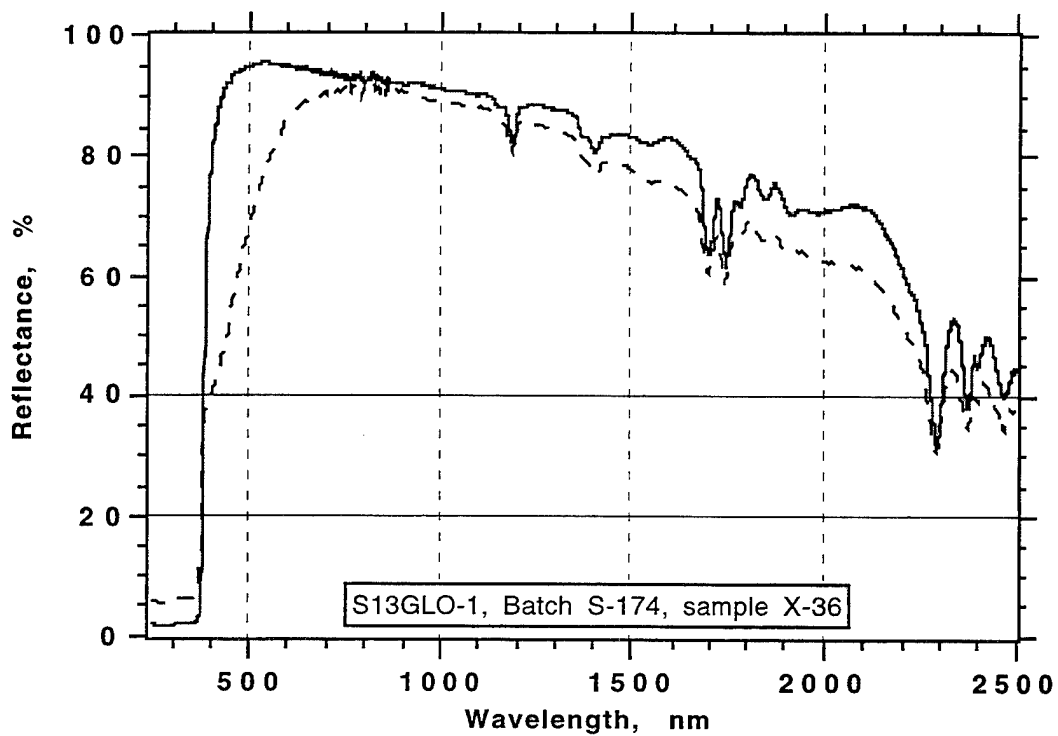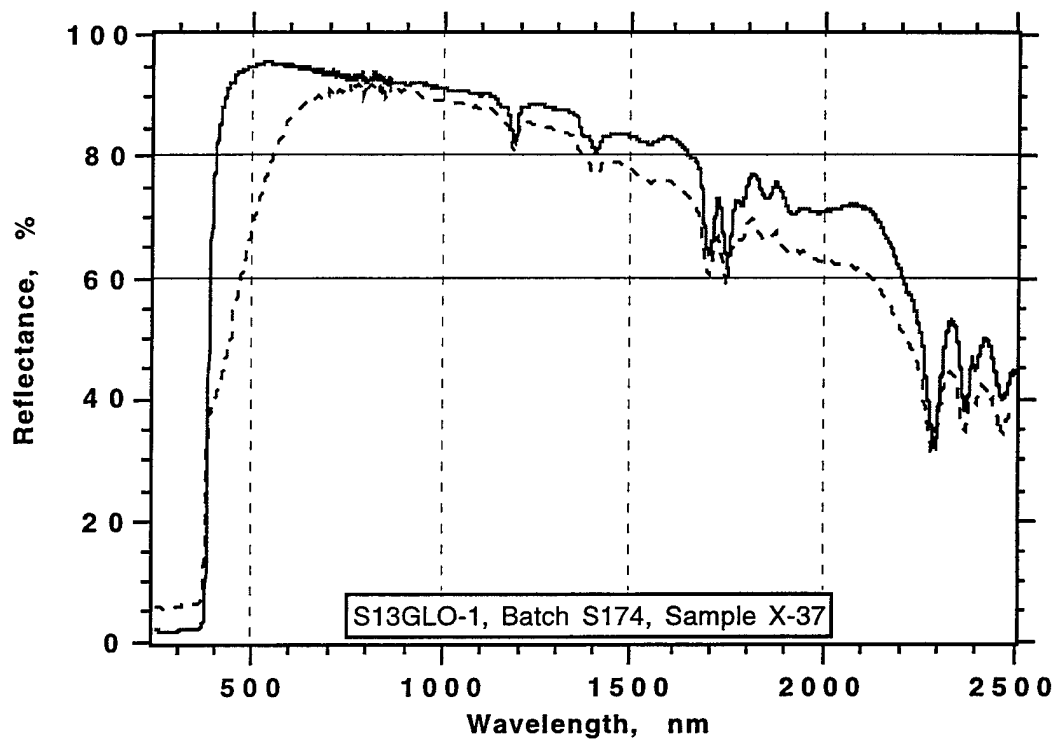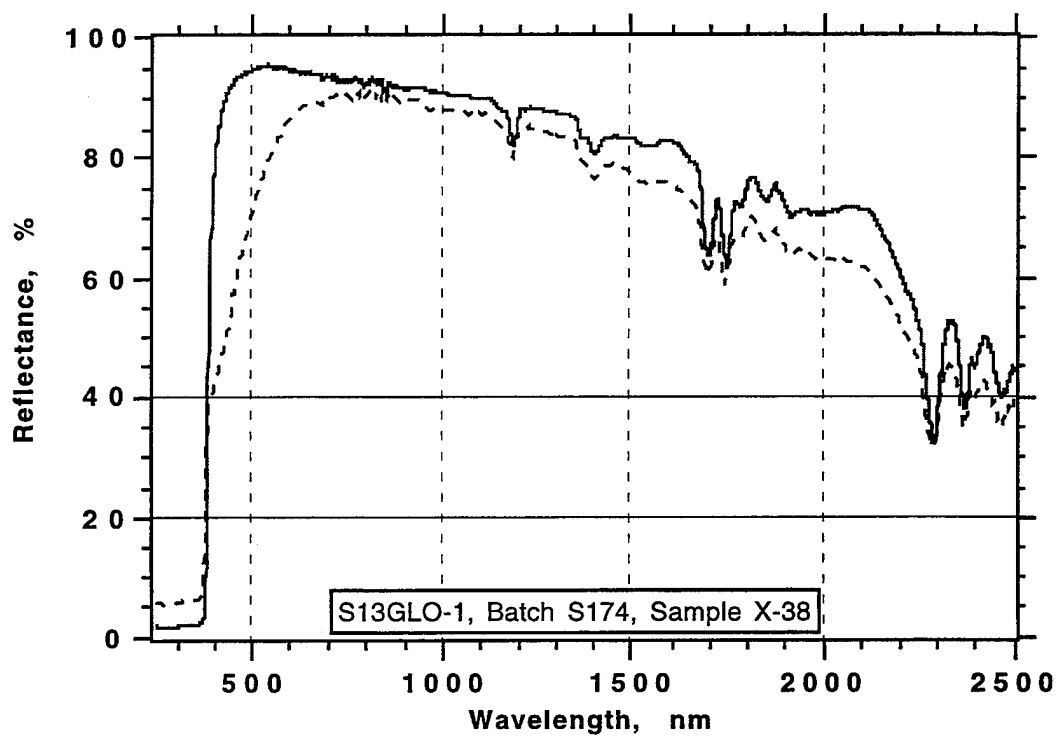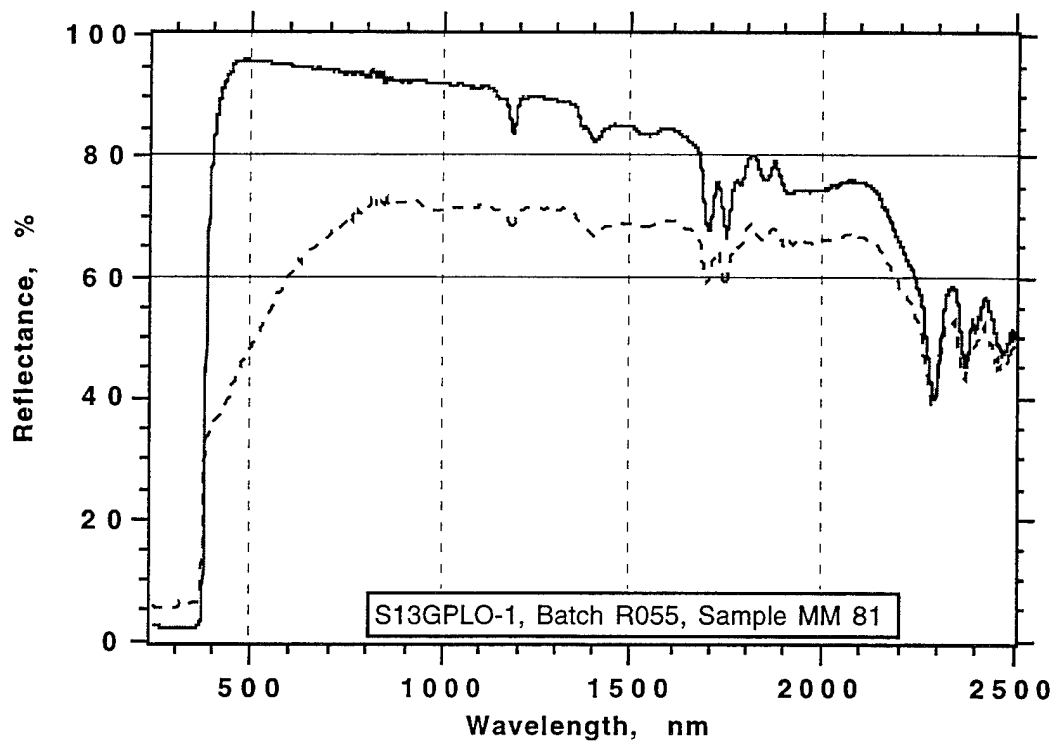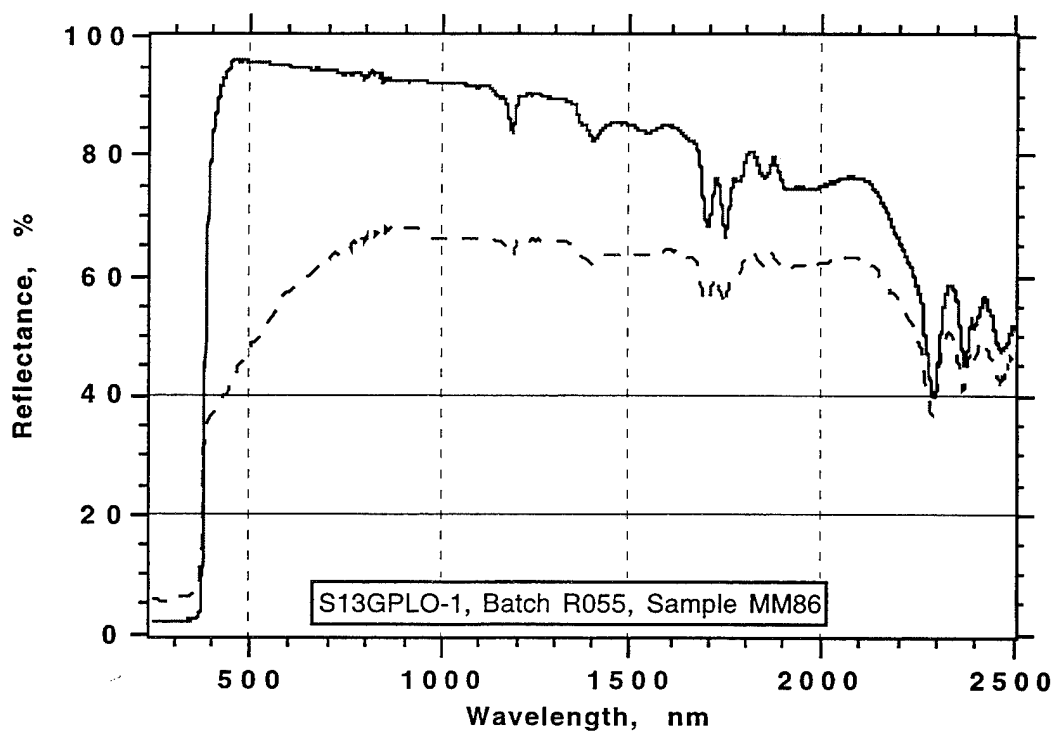
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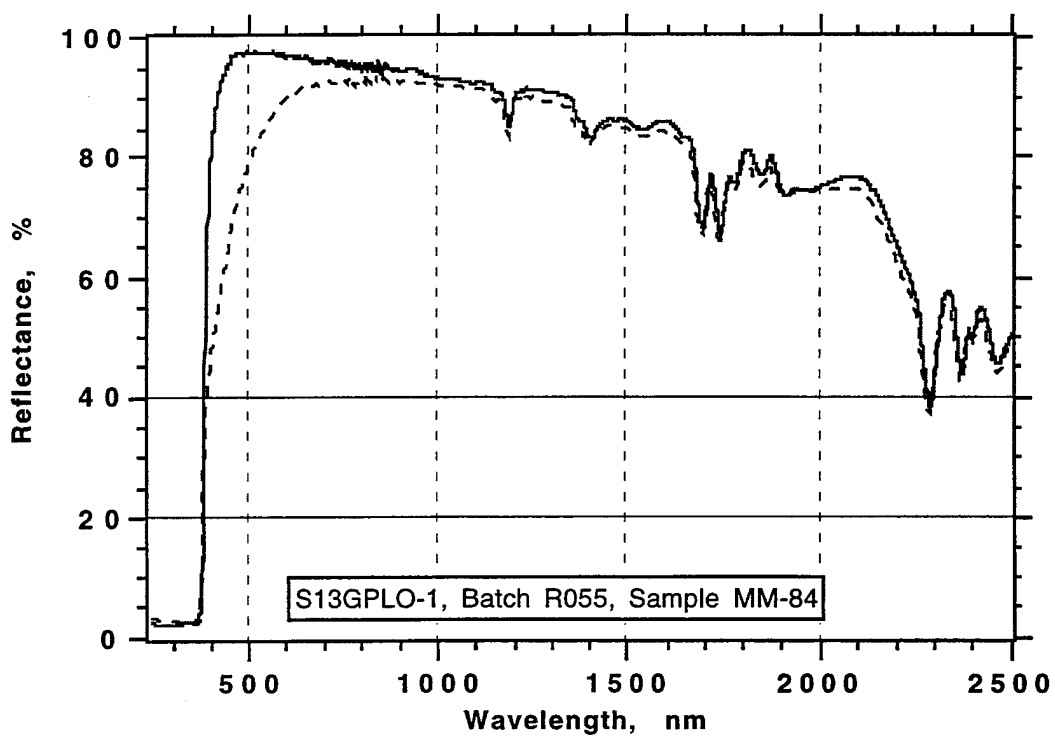
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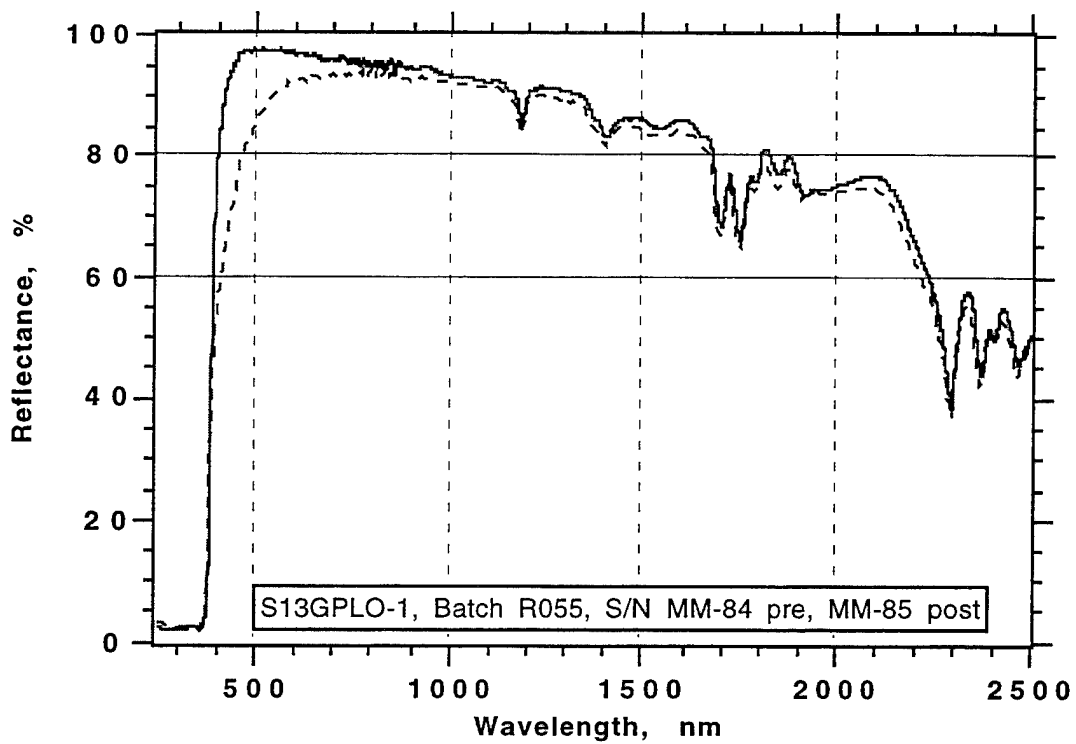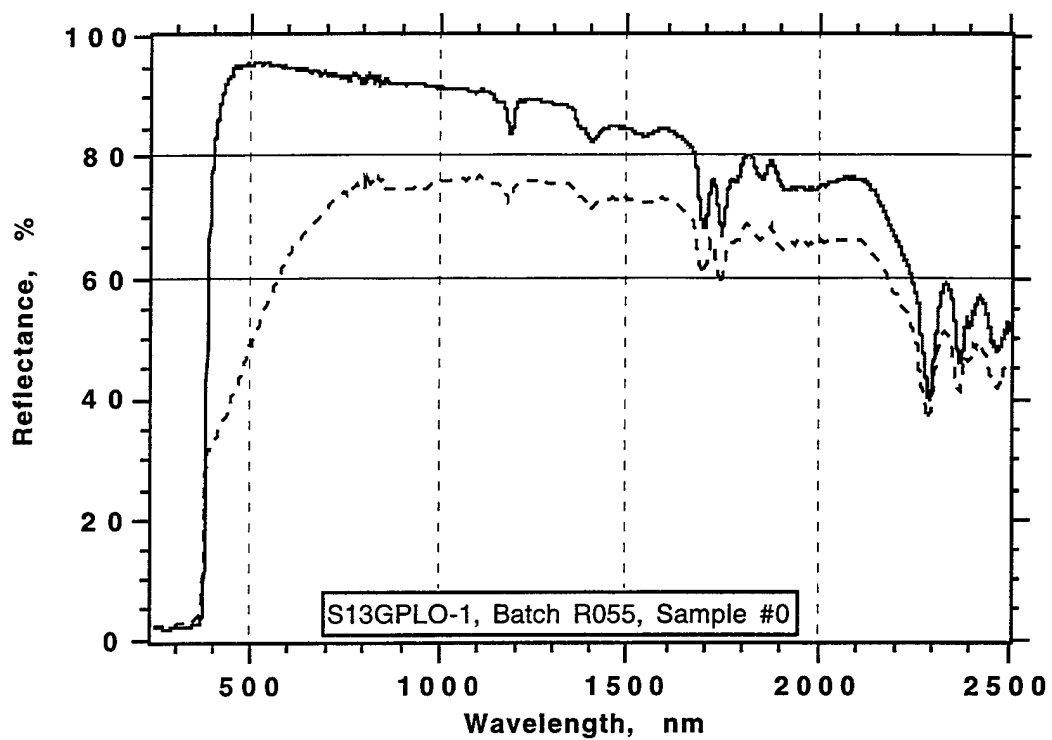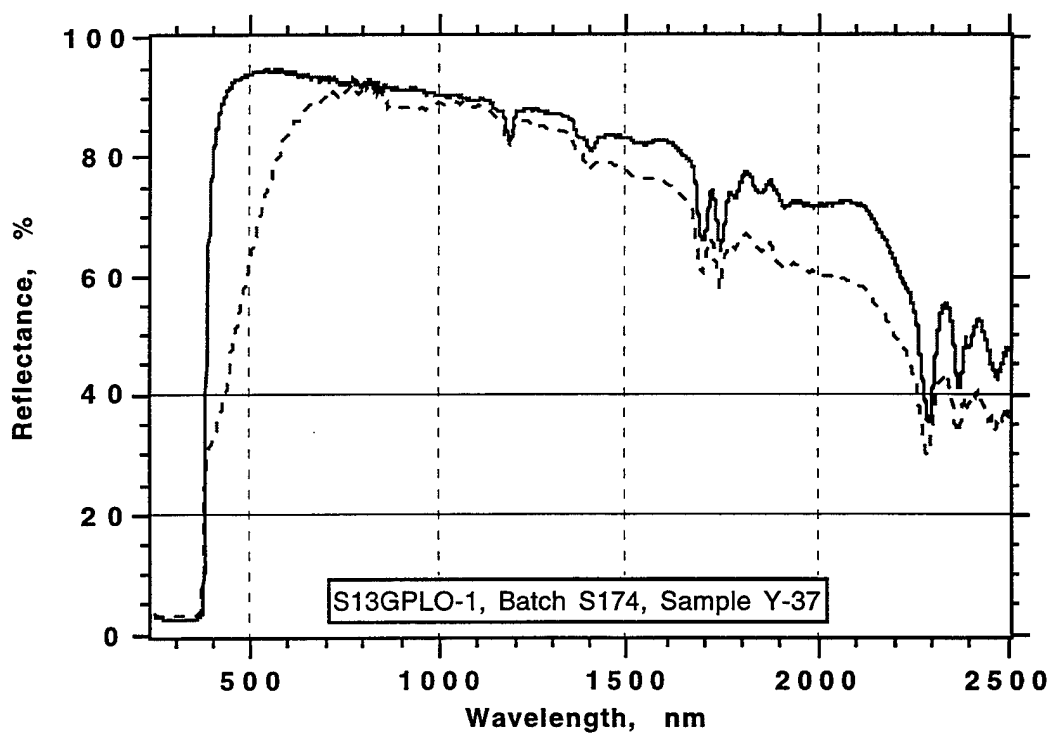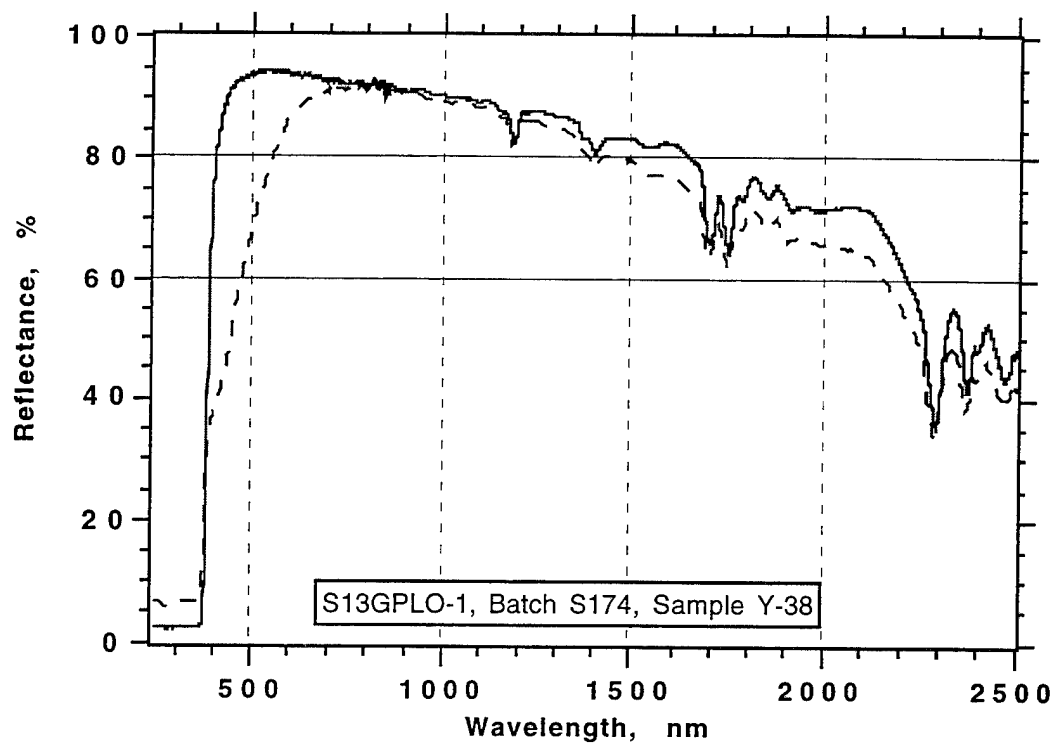
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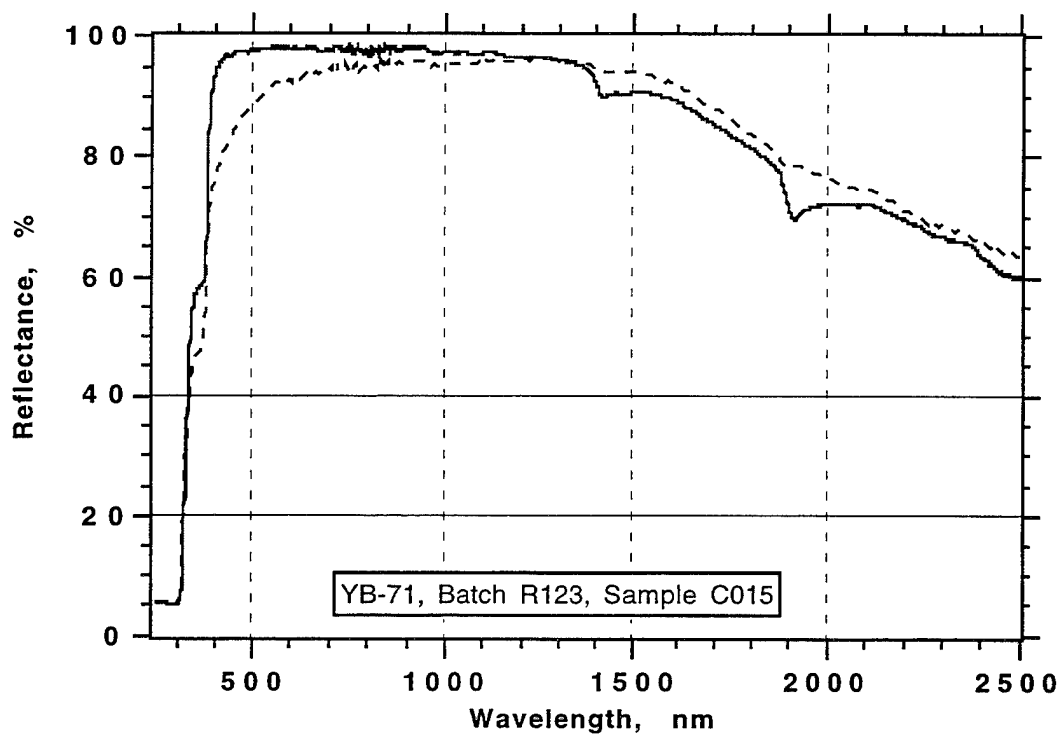
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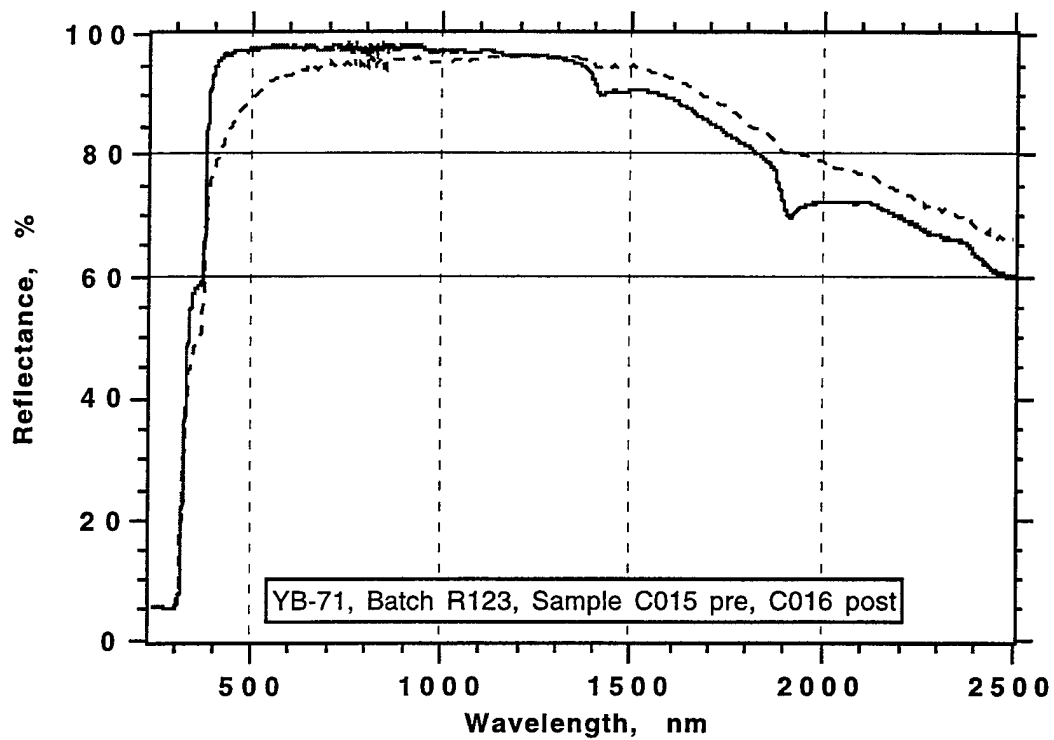
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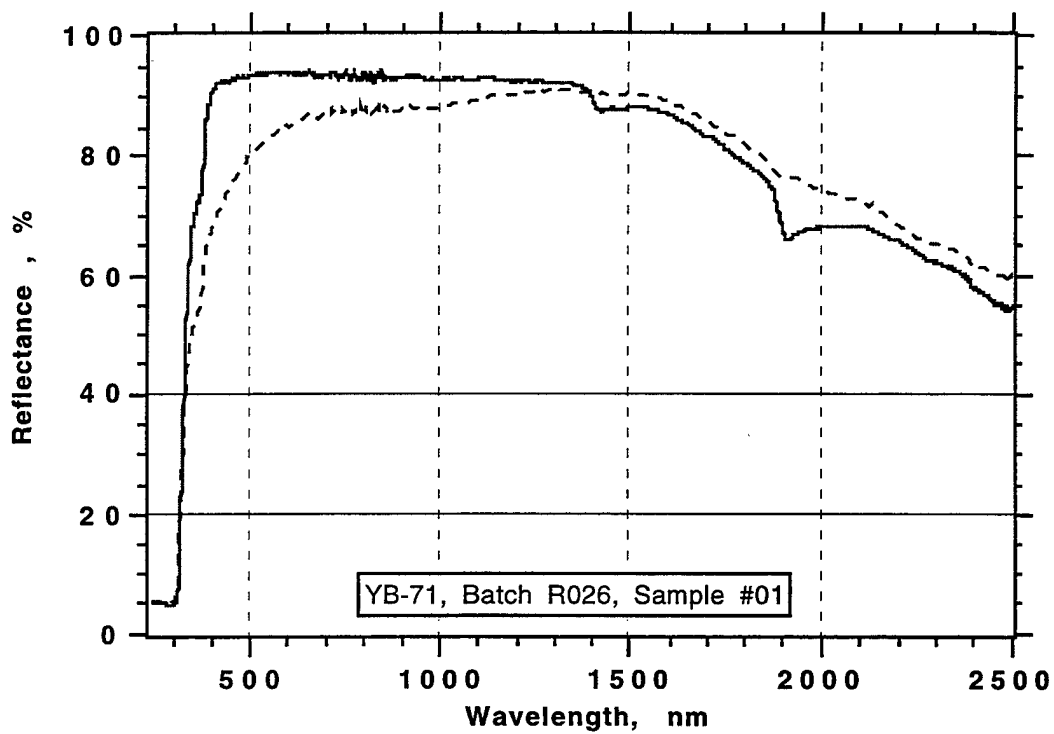
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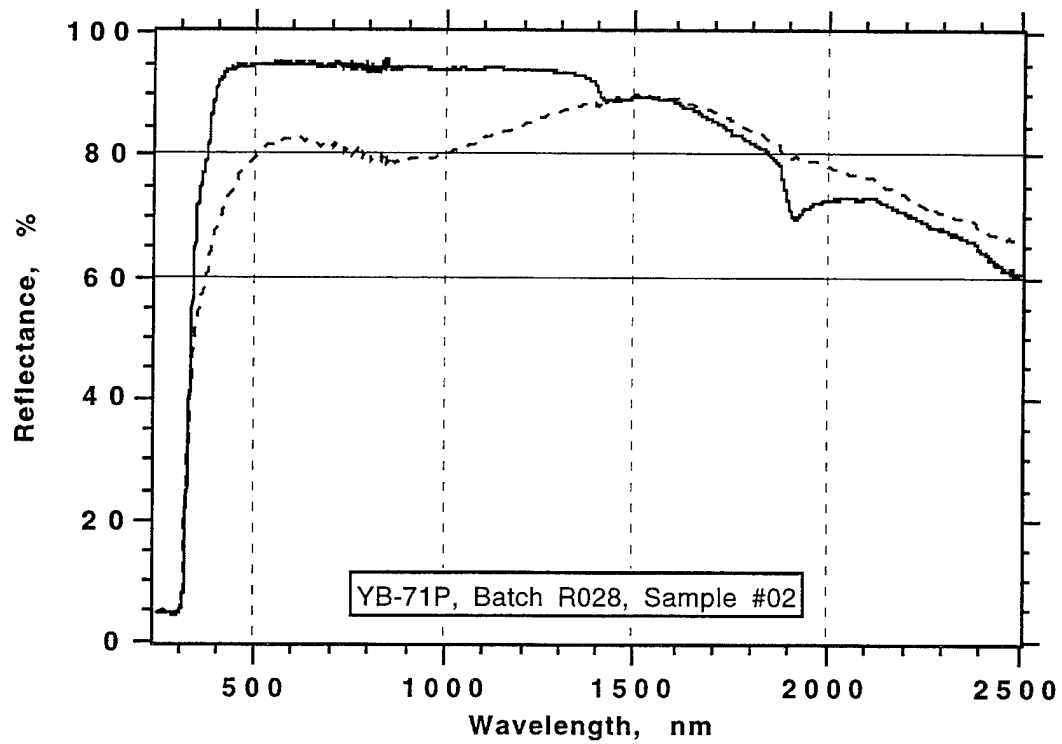
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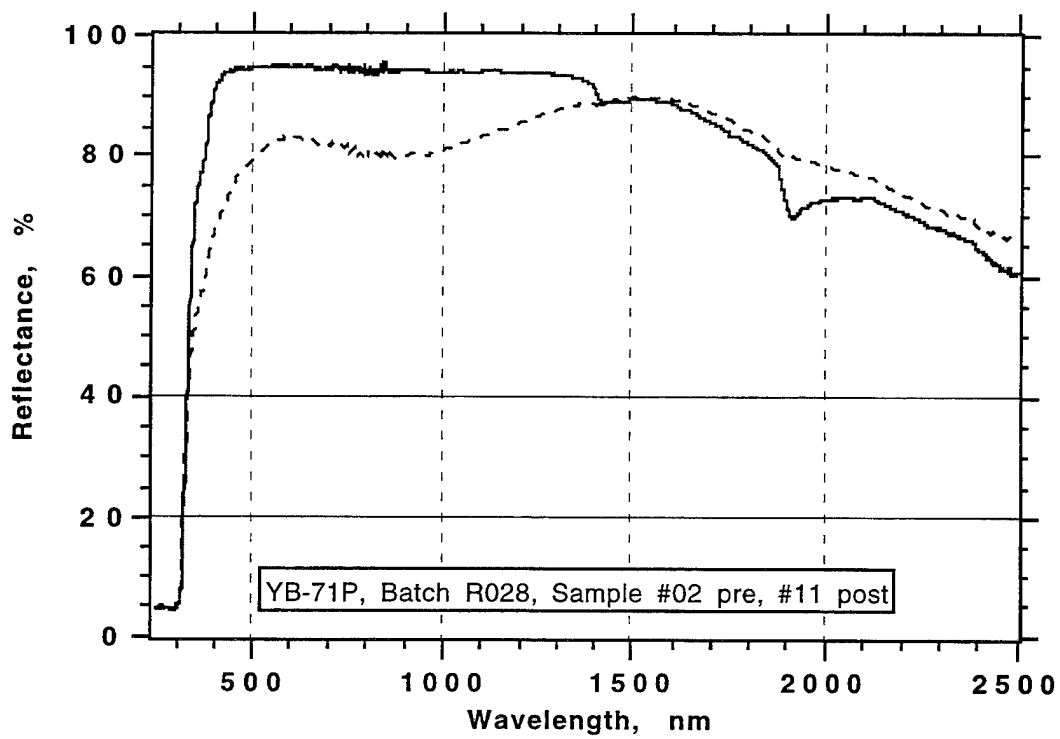
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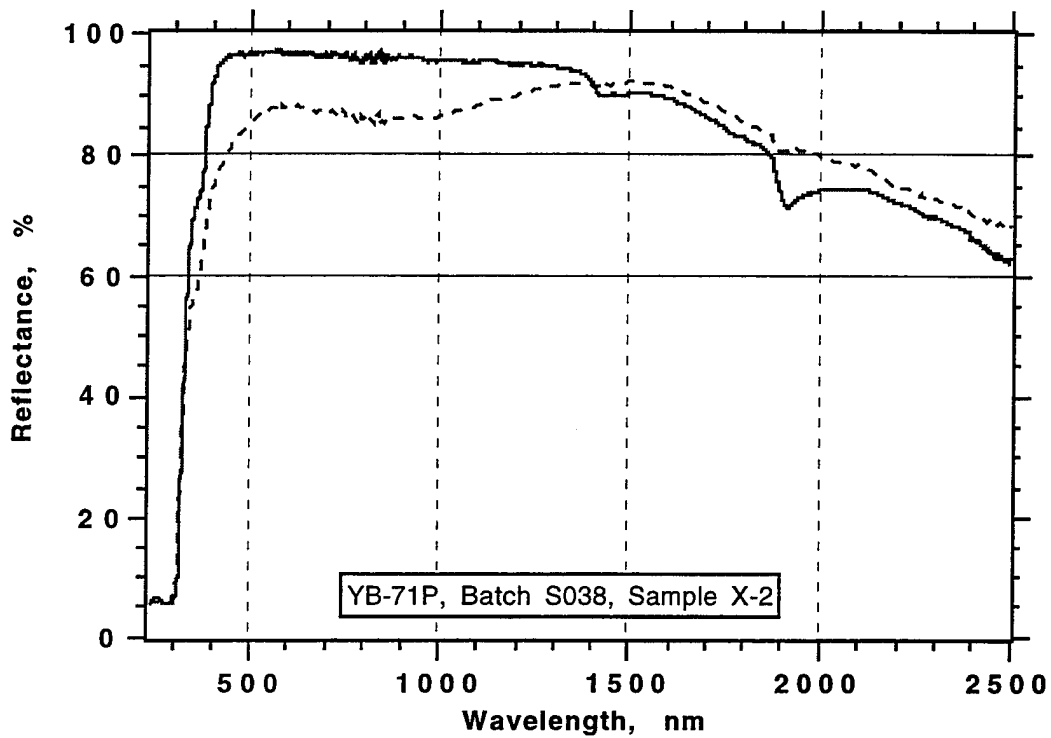
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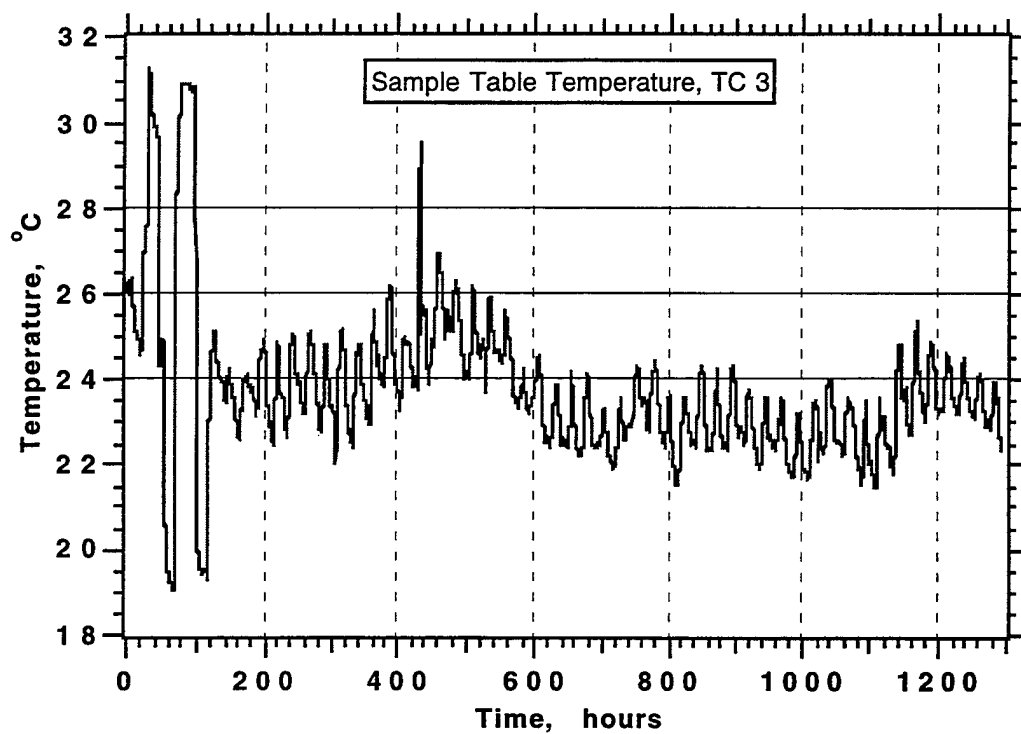
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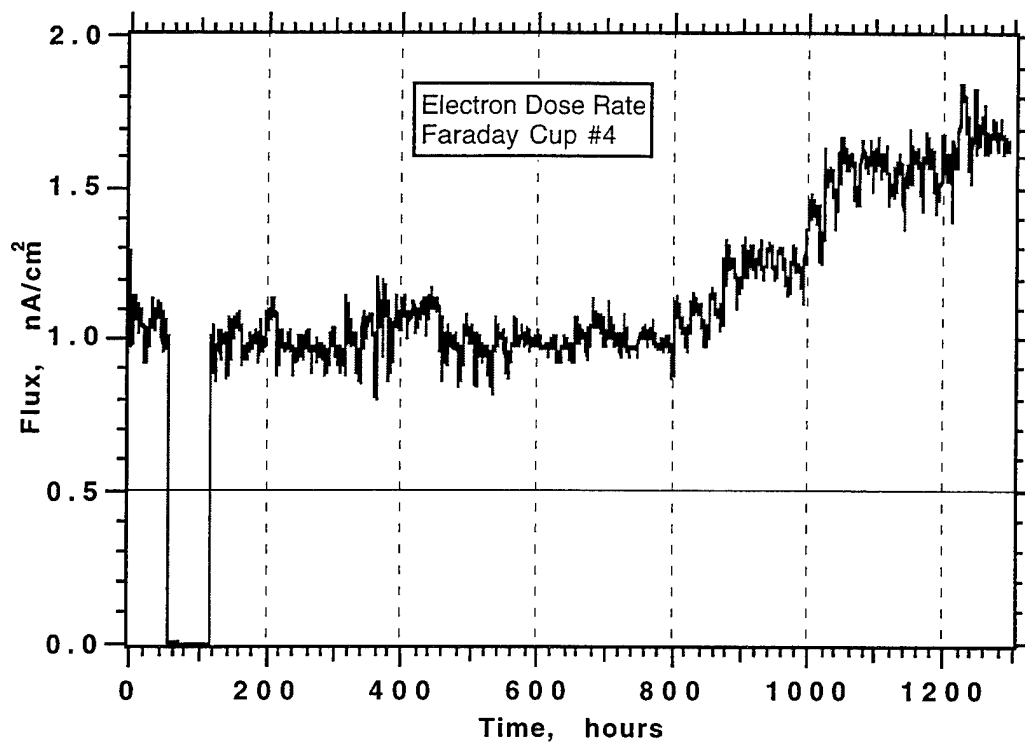
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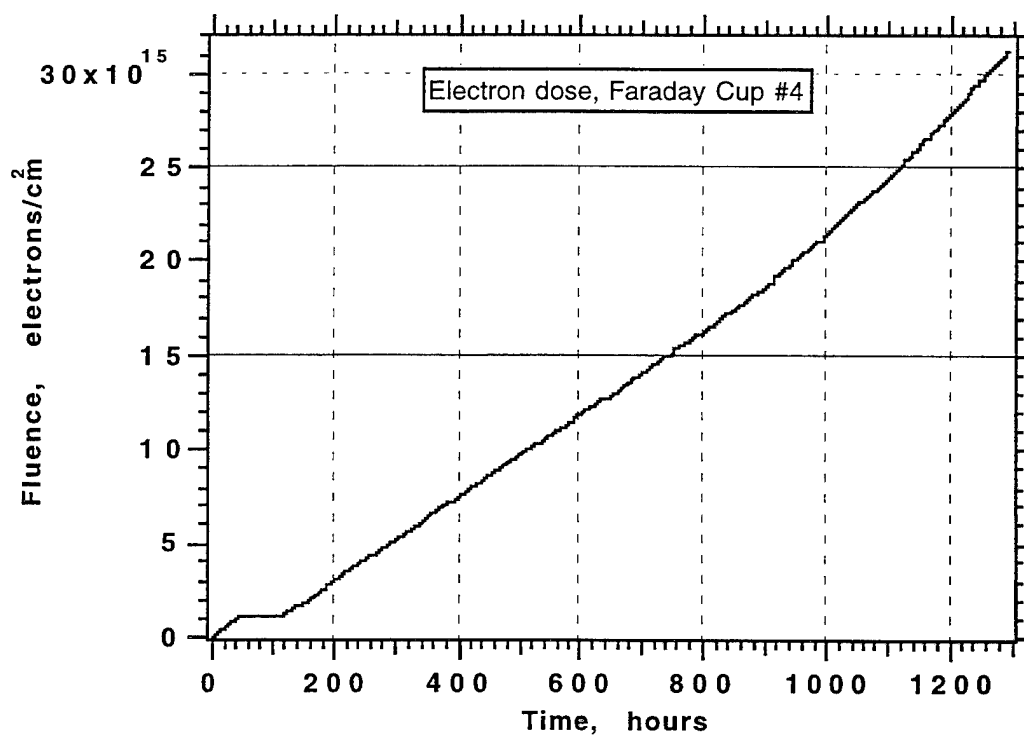
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YB-71, Batch P062, #2, α_s= 0.091 pre-, 0.201 post-

Graph 23

YB-71, Batch Q051, #1, α_s= 0.103 pre-, 0.199 post-

Graph 24

YB-71, Batch Q051, #2, α_s= 0.105 pre-, 0.200 post-

Graph 25.

YB-71, Batch R123, C001, α_s= 0.082 pre-, 0.211 post-

Graph 26.

YB-71, Batch R123, C014, α_s= 0.079 pre-, 0.224 post-

Graph 27.

YB-71, Batch R026, #2, α_s= 0.137 pre-, 0.312 post-

Graph 28.

YB-71, Batch R026, #3, α_s= 0.125 pre-, 0.319 post-

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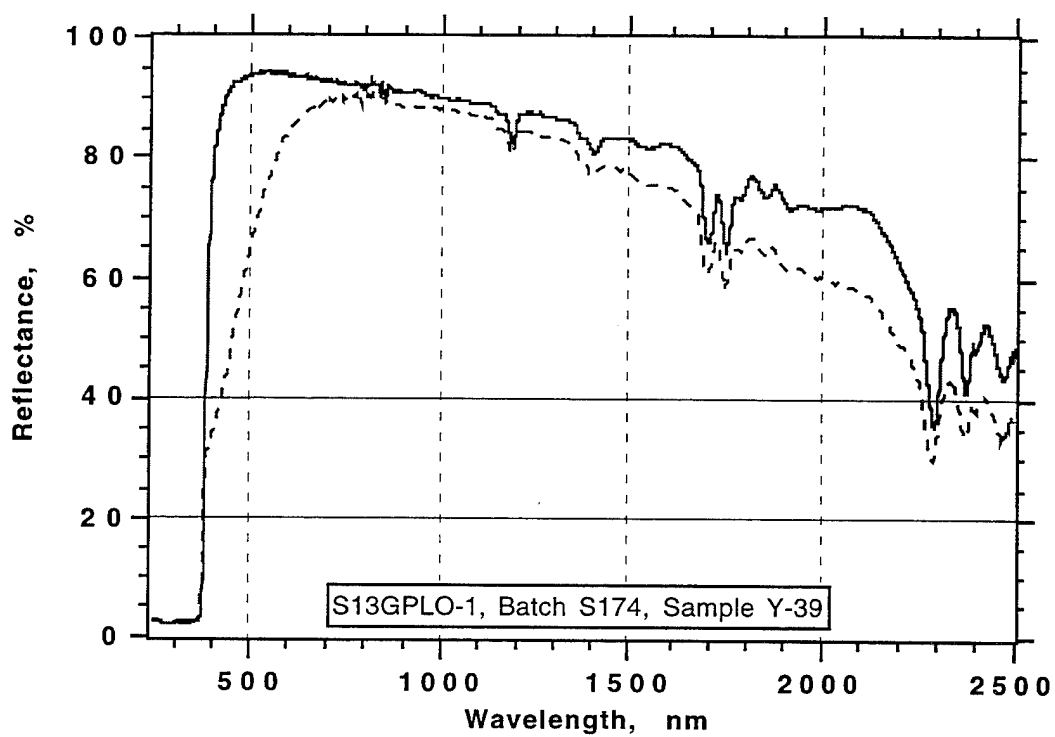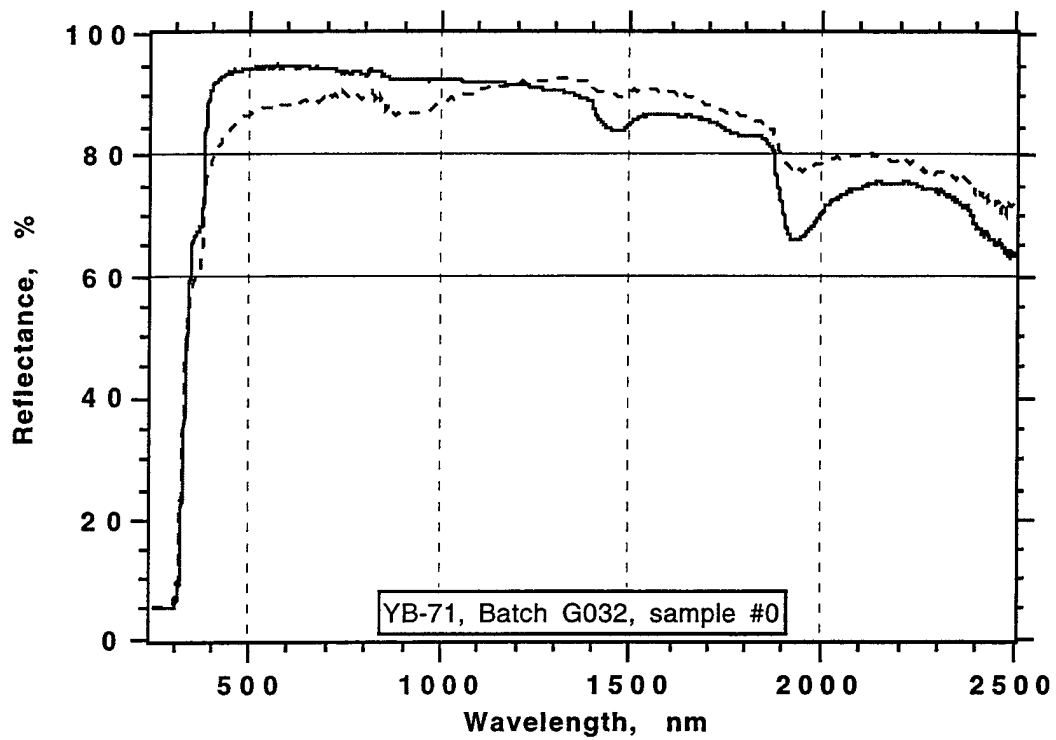YB-71P, Batch R028, #5, α_s= 0.102 pre-, 0.377 post-
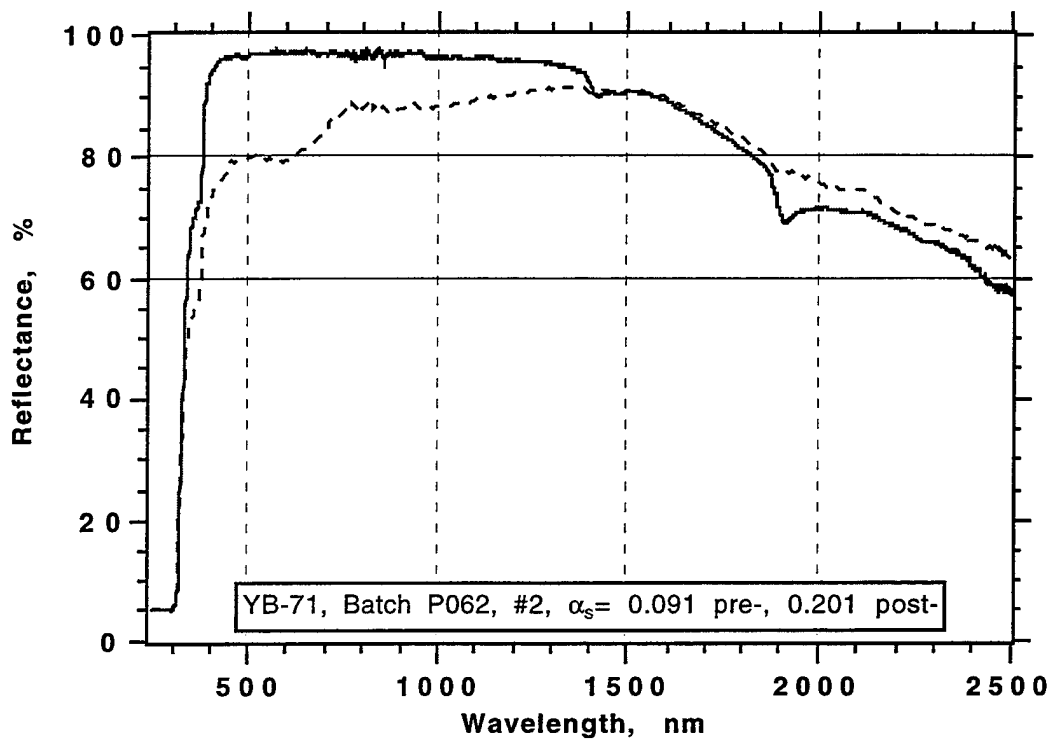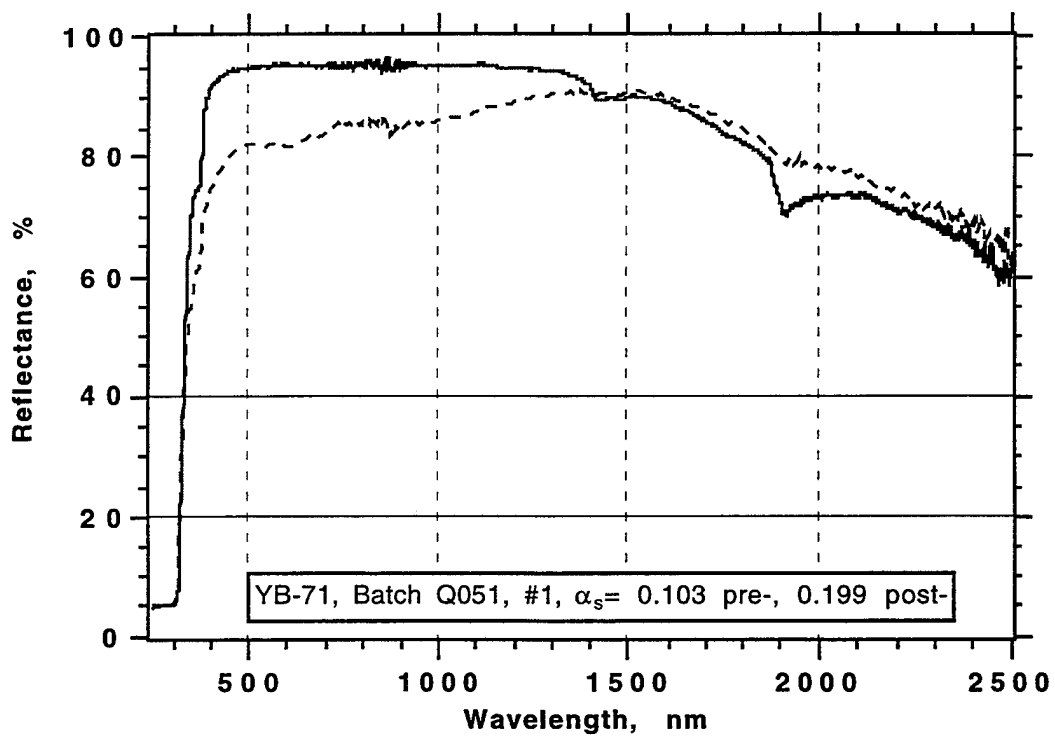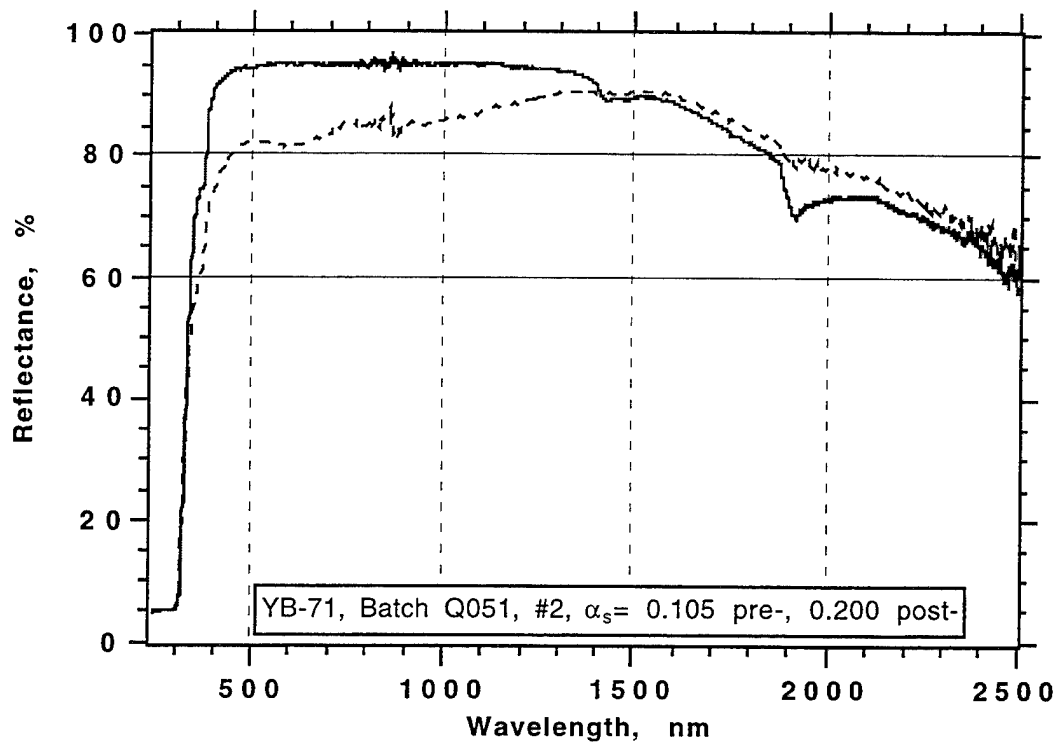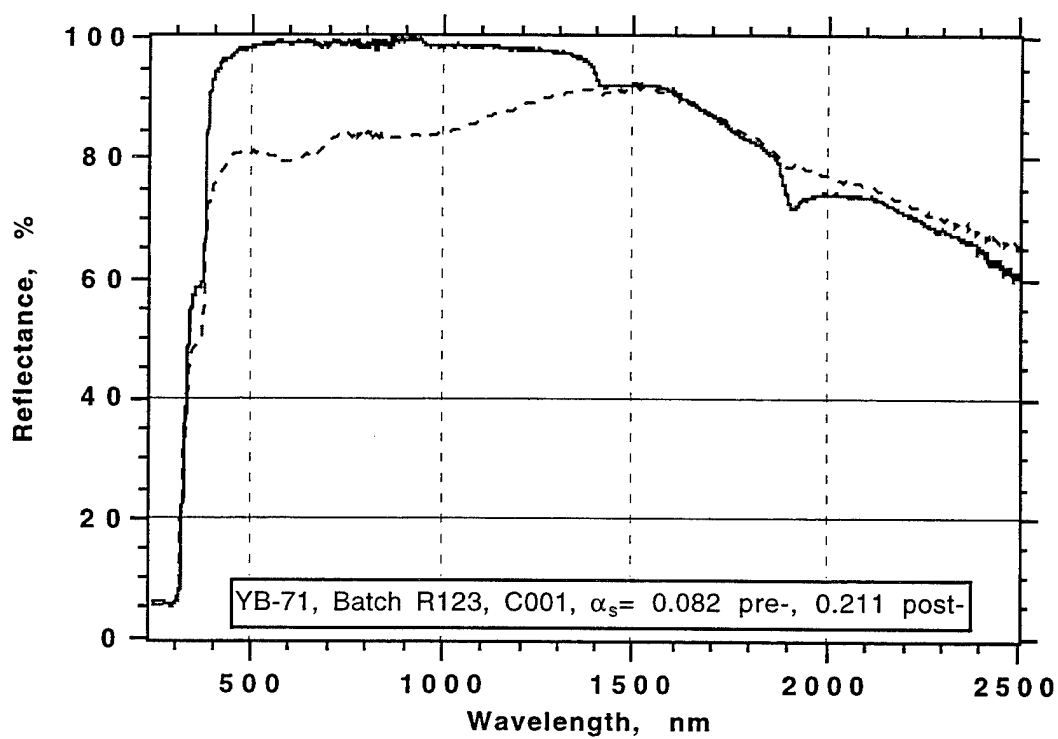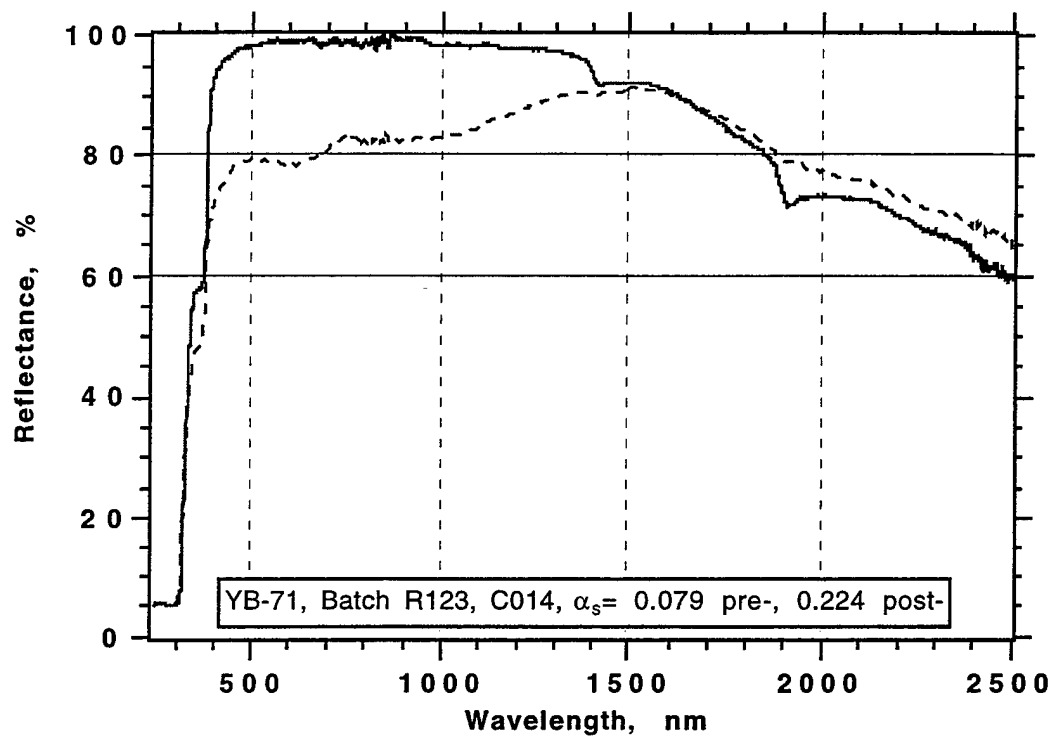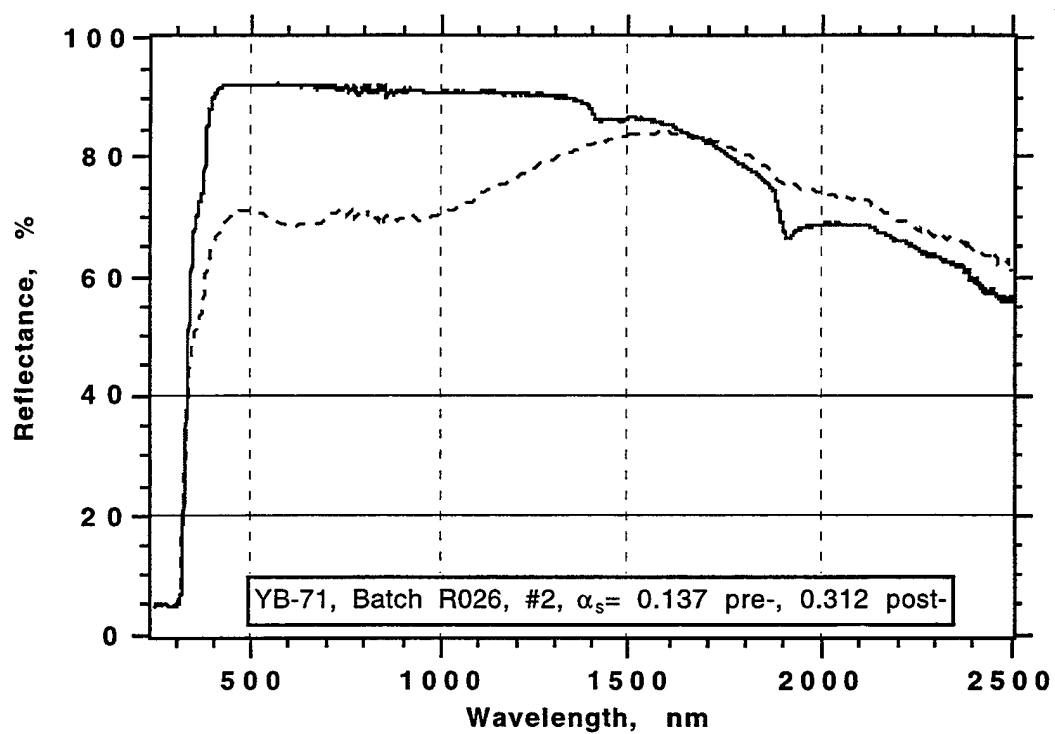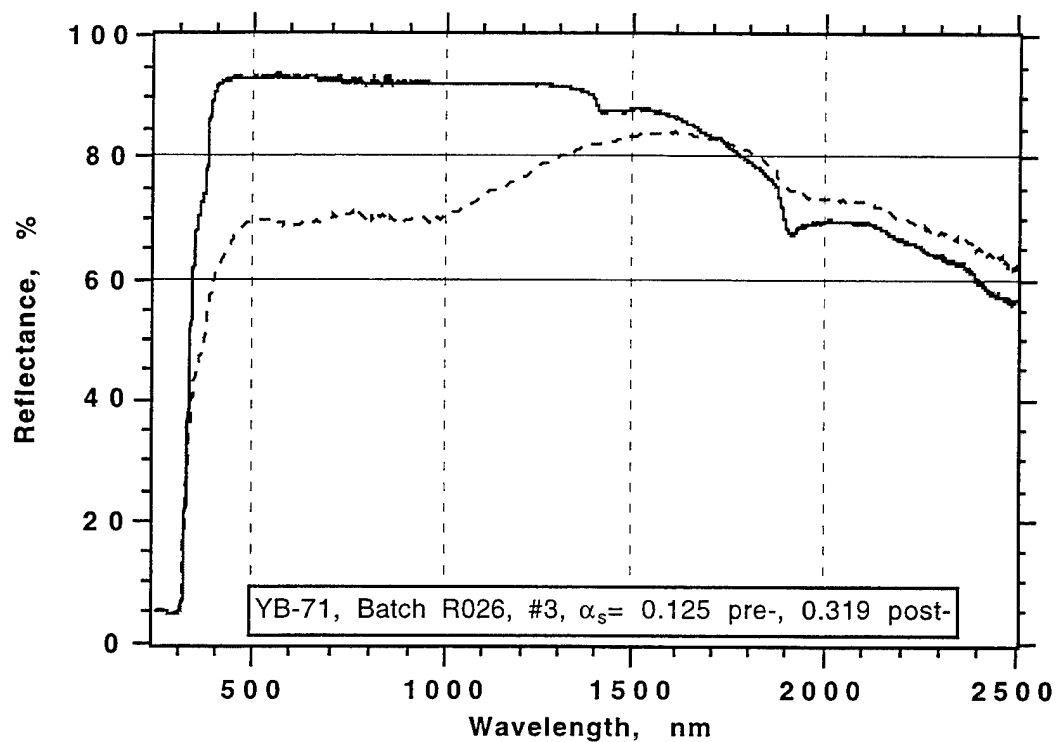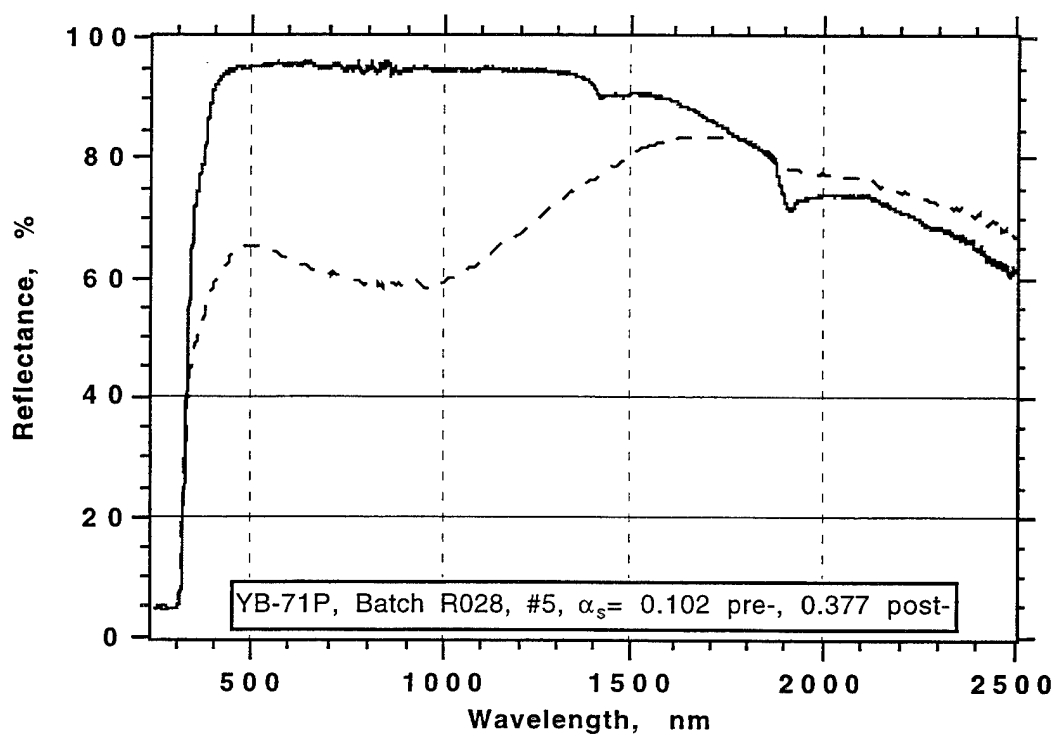
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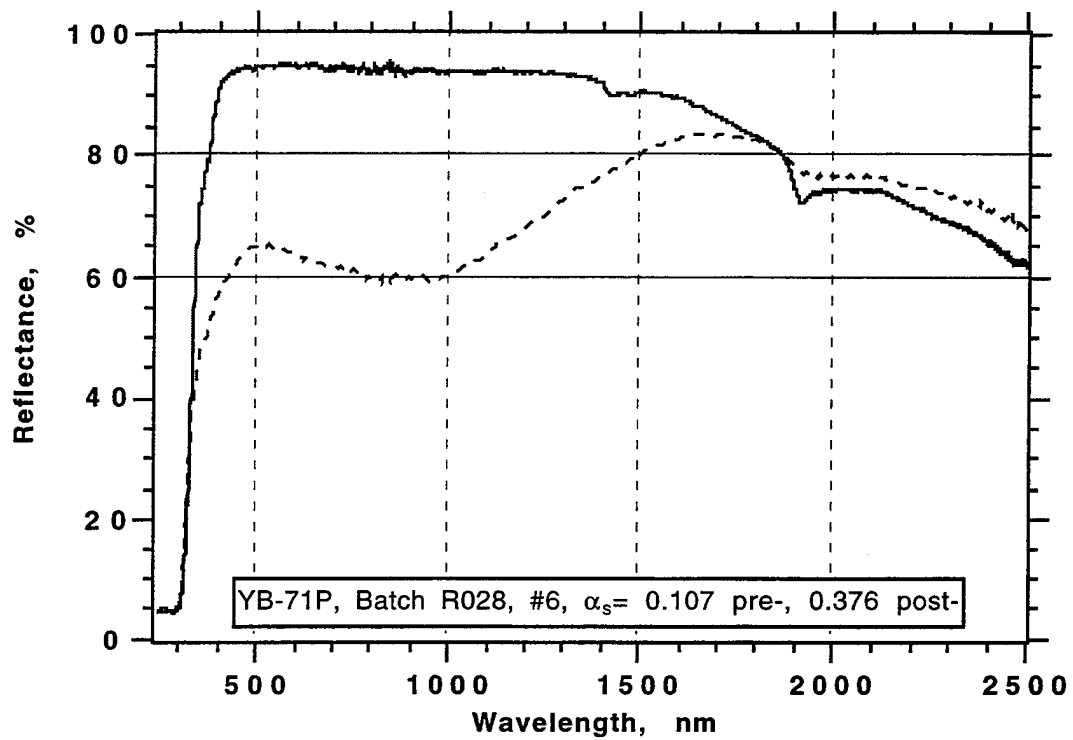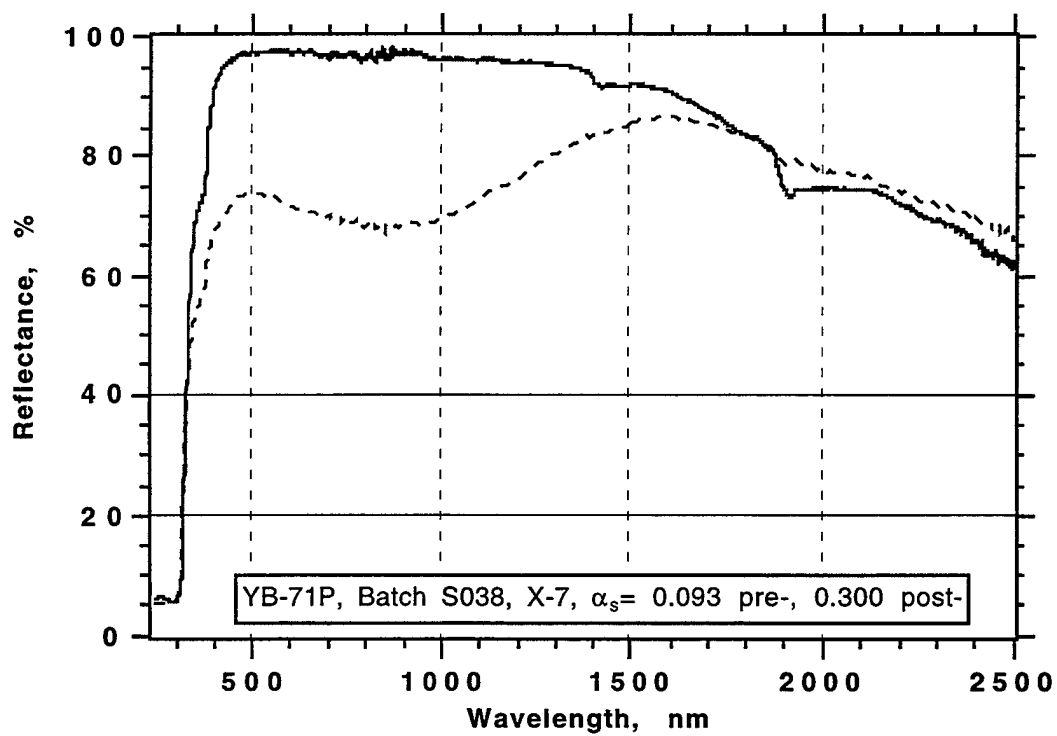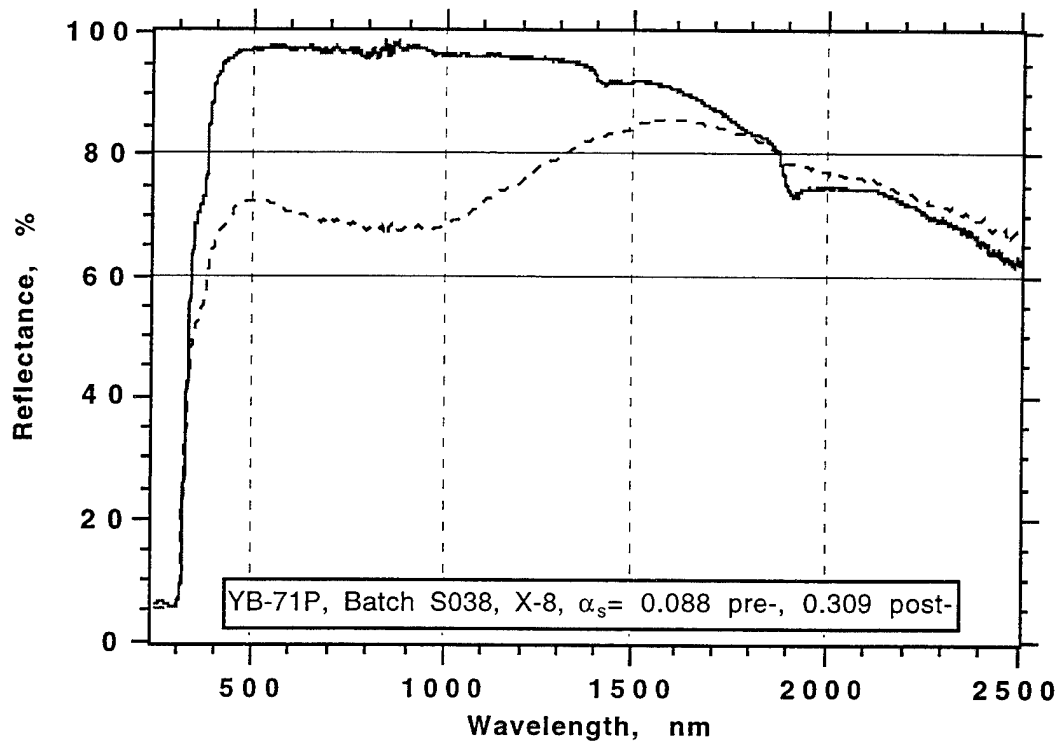
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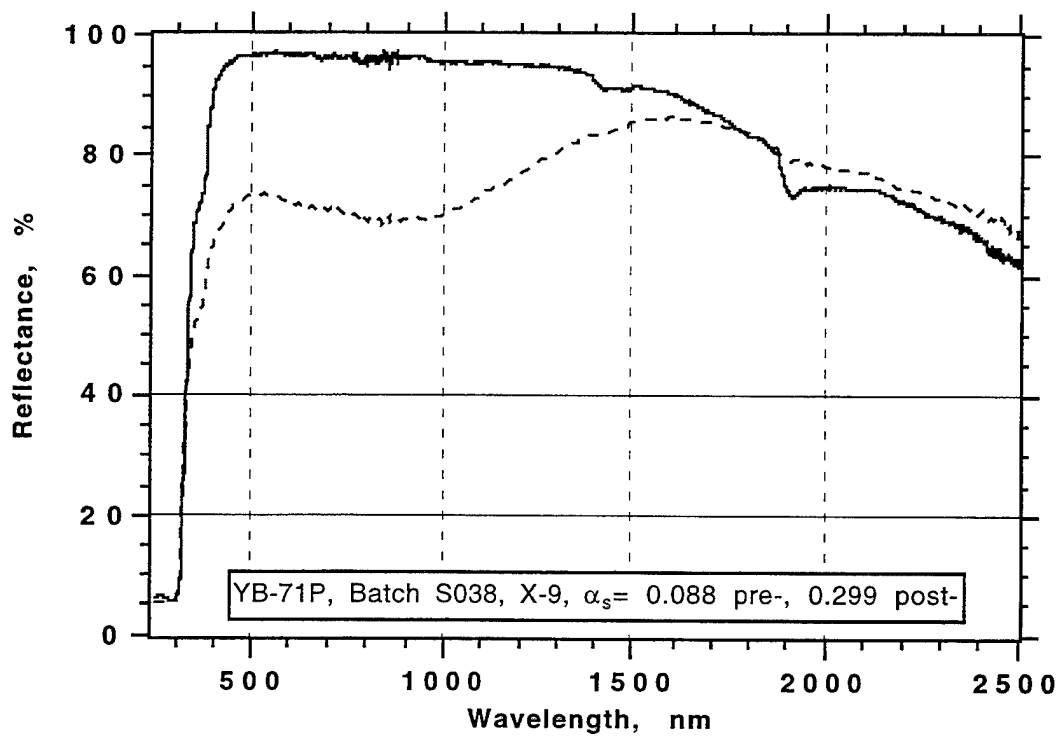
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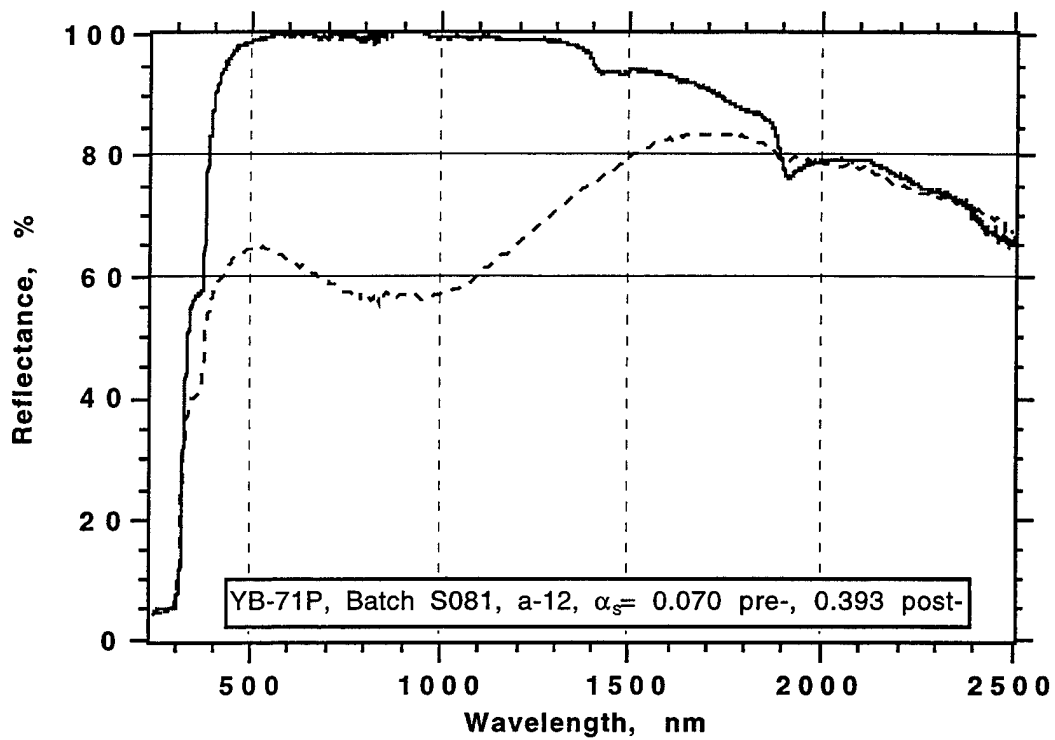
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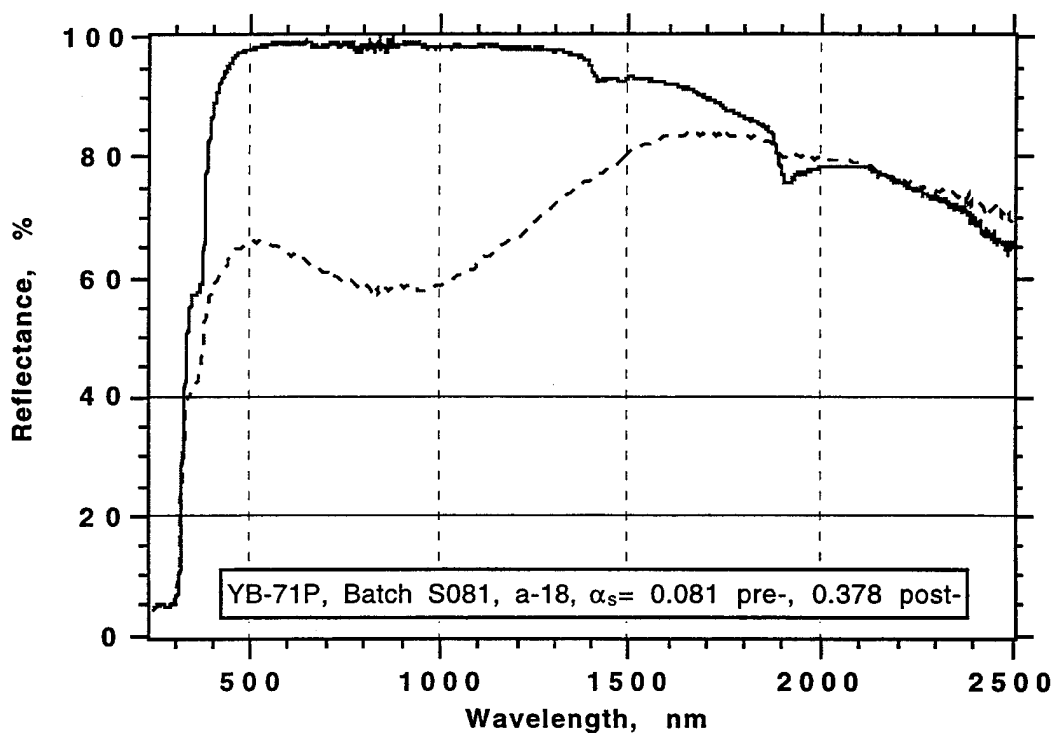
Graph 36.

Graph 37.

Graph 38.

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Z-93, Batch G028, #2, α_s= 0.138 pre-, 0.192 post-

Graph 39.

Z-93, Batch G028, #3, α_s= 0.133 pre-, 0.222 post-

Graph 40.

YB-71/P: ZOTTEST DATA

Graph 41.

Graph 42.

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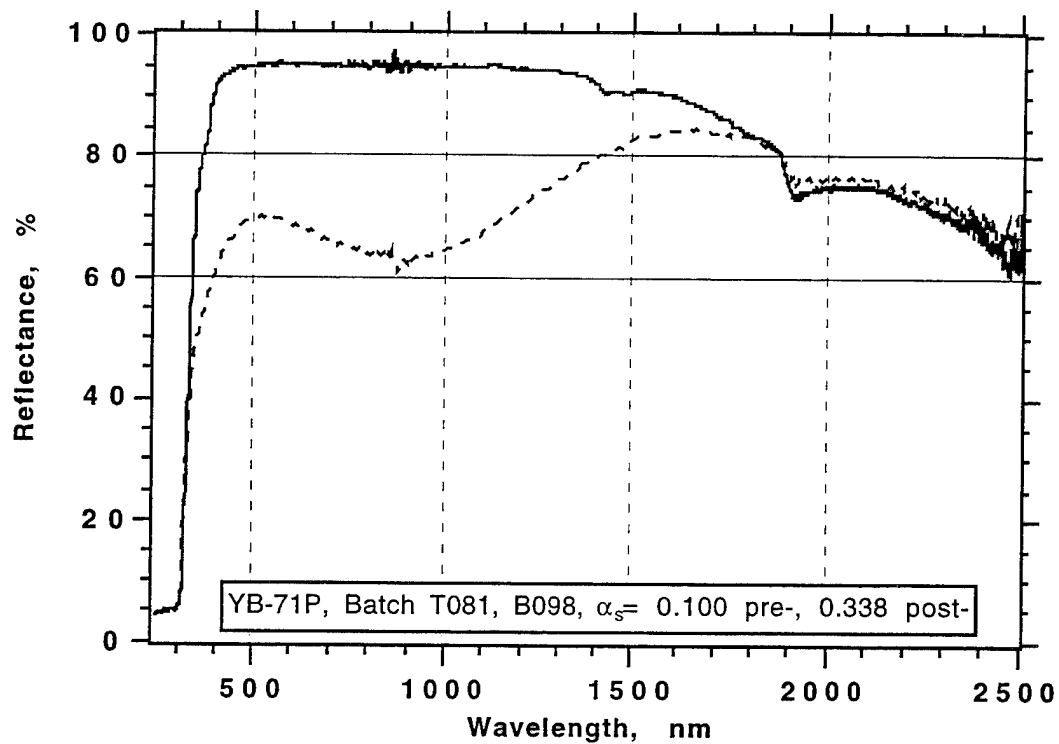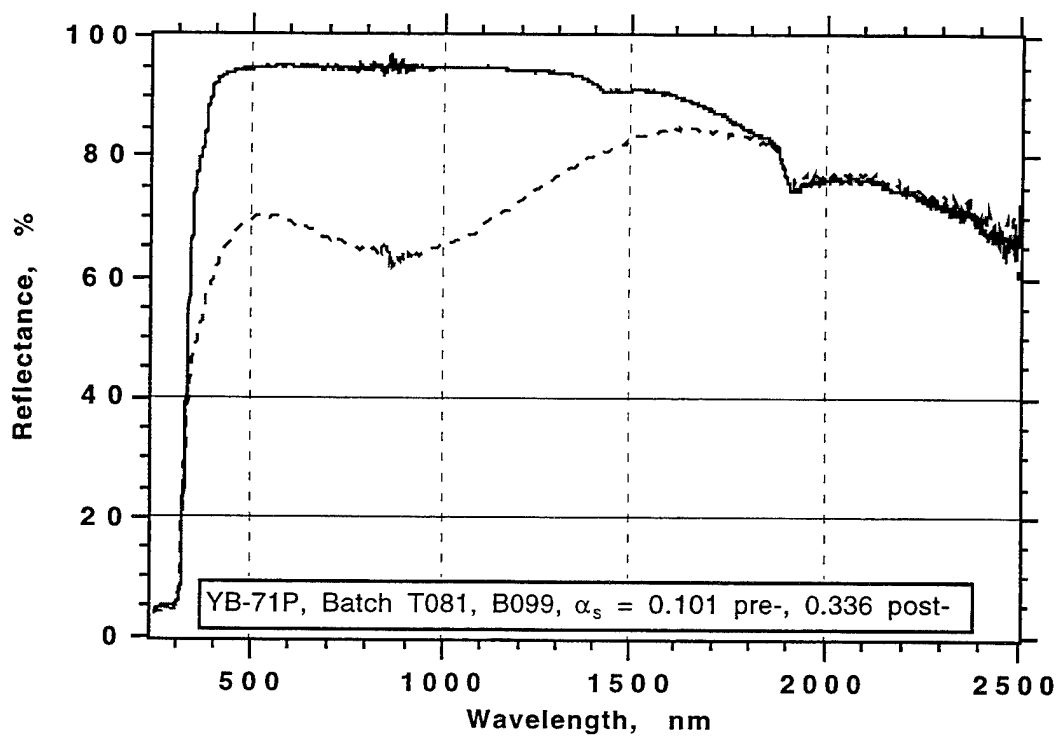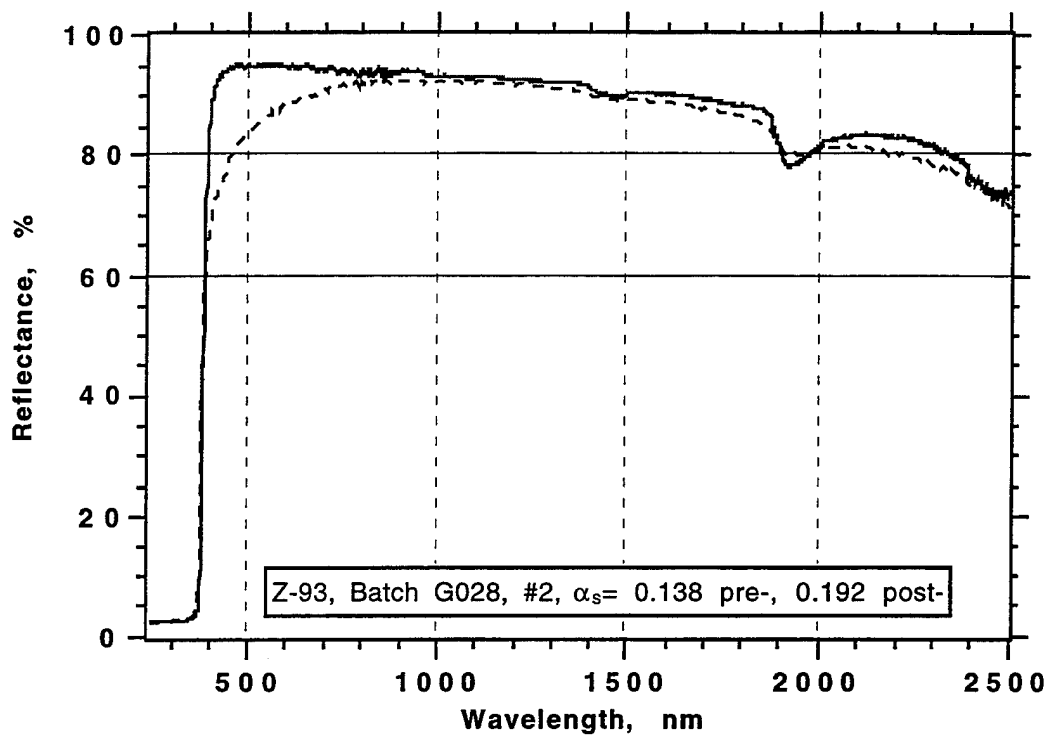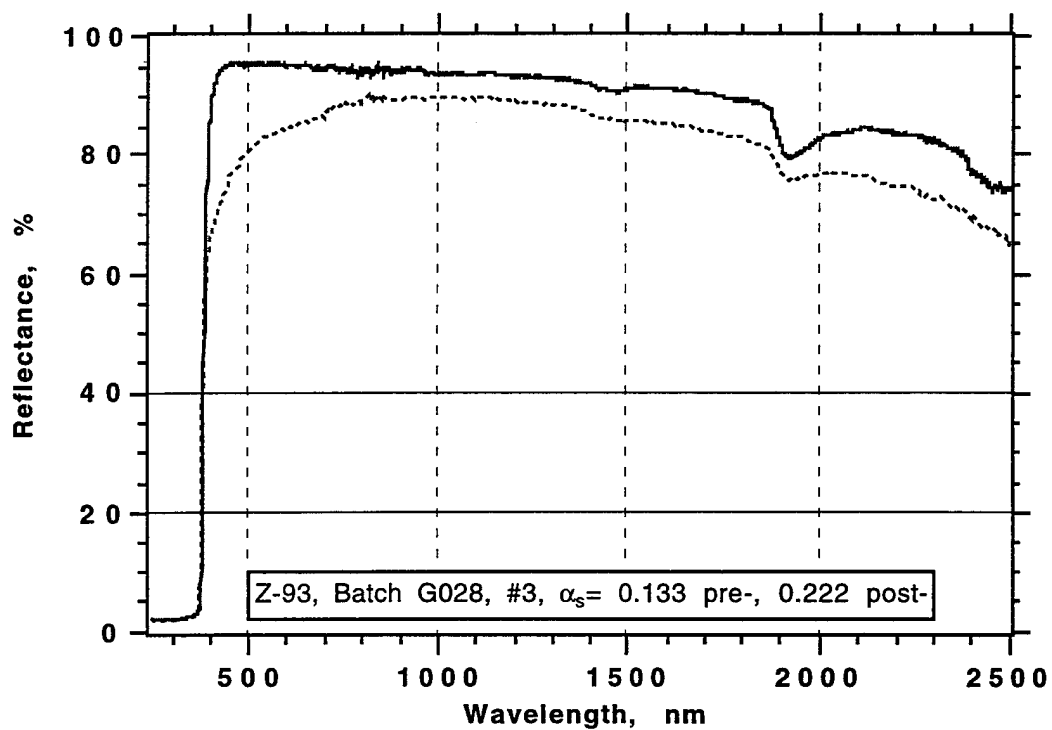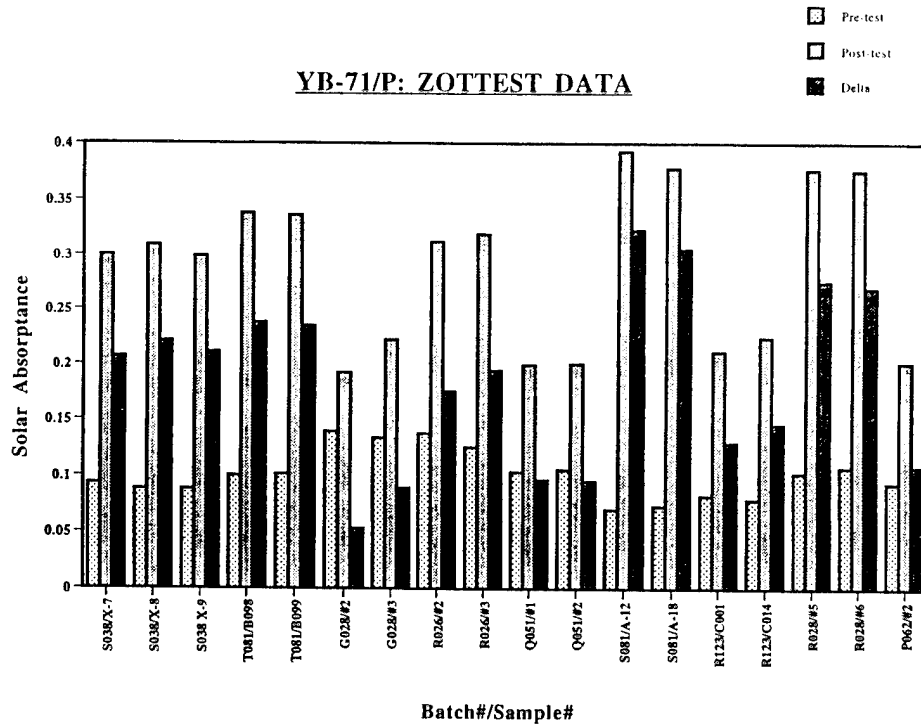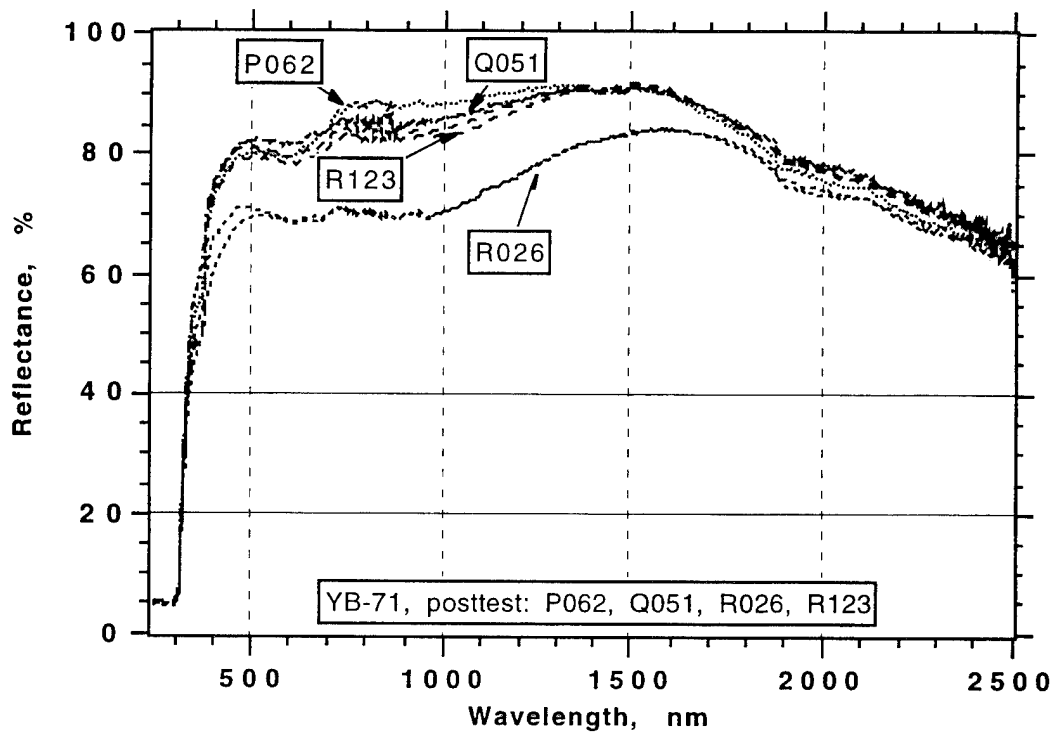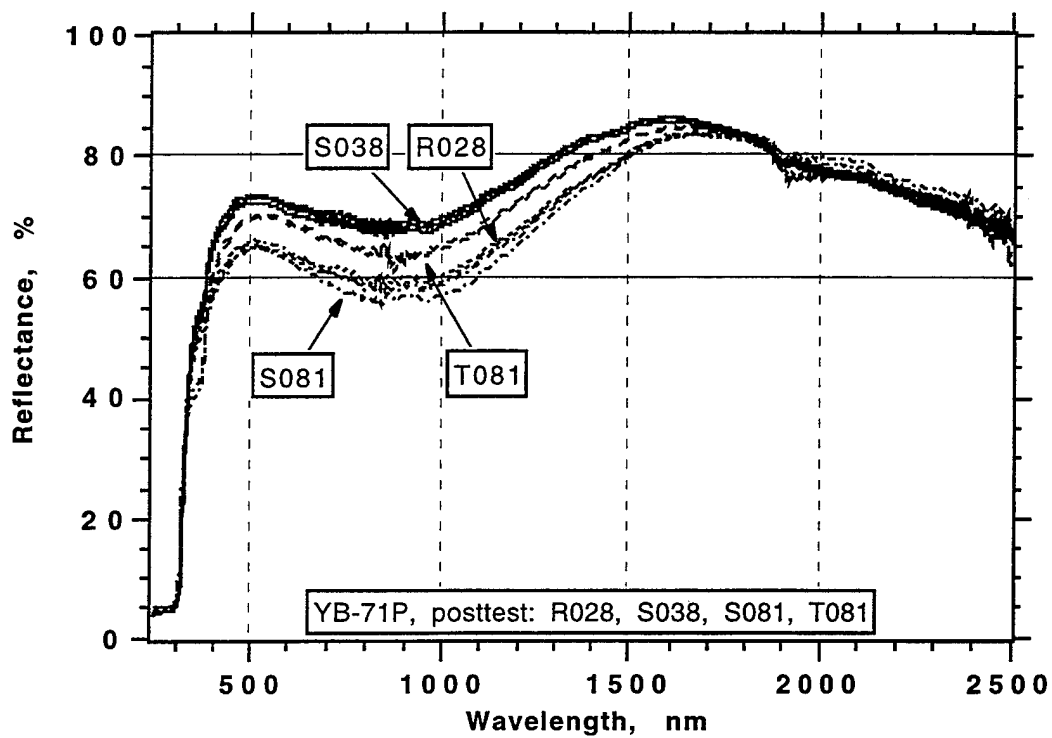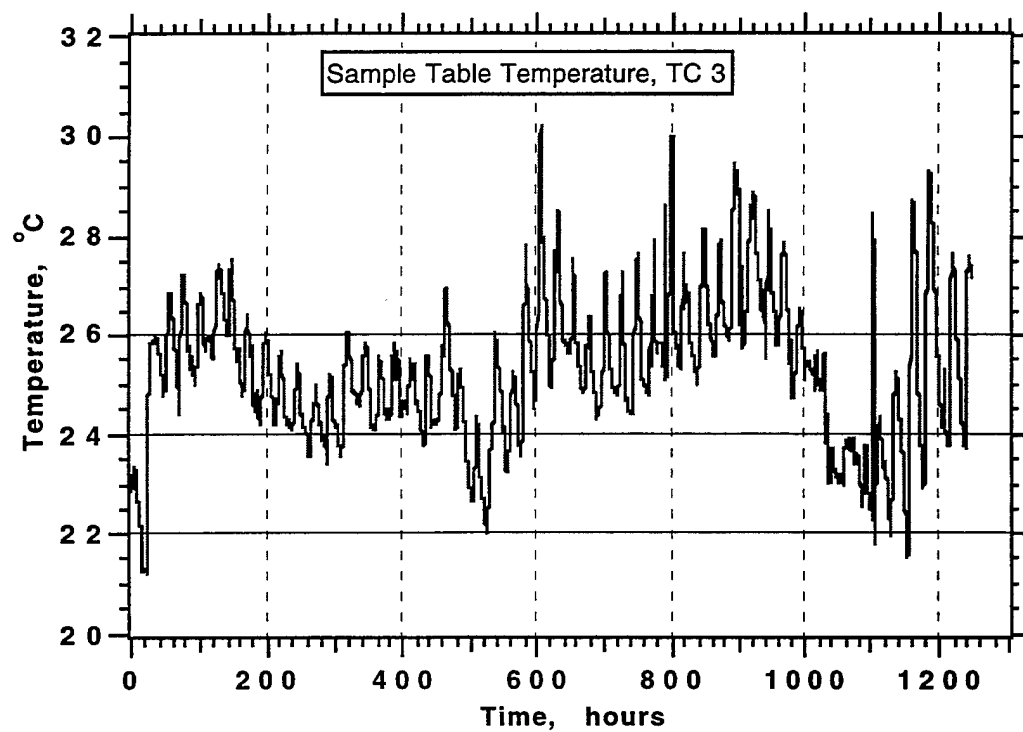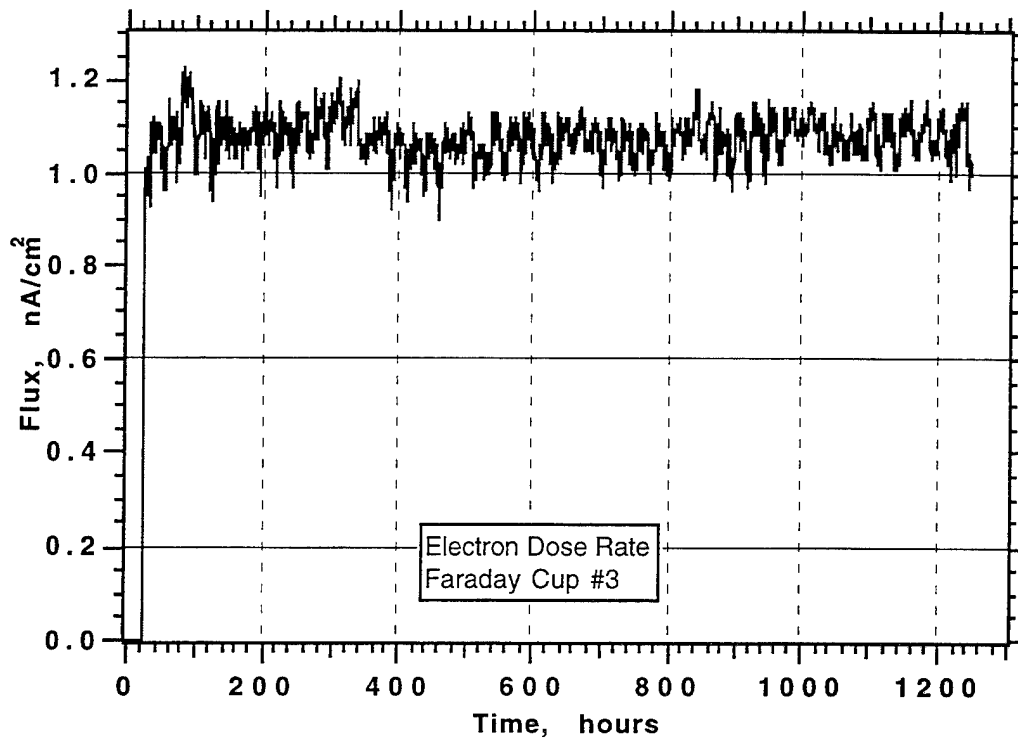
Graph 43.

Graph 44.

Graph 45.
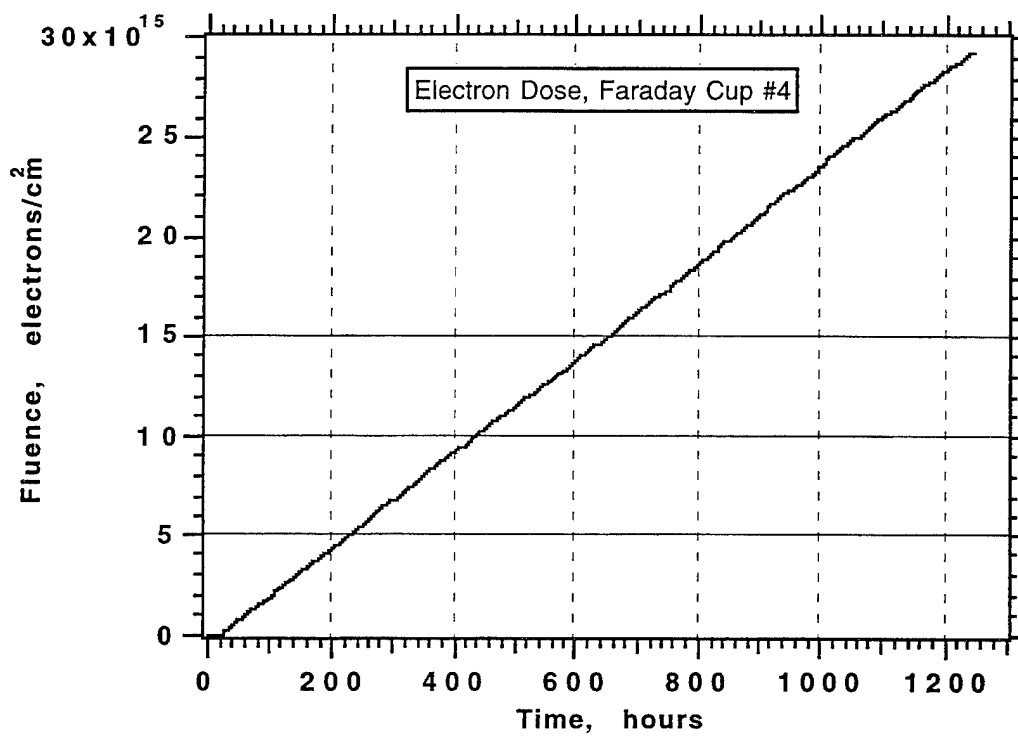
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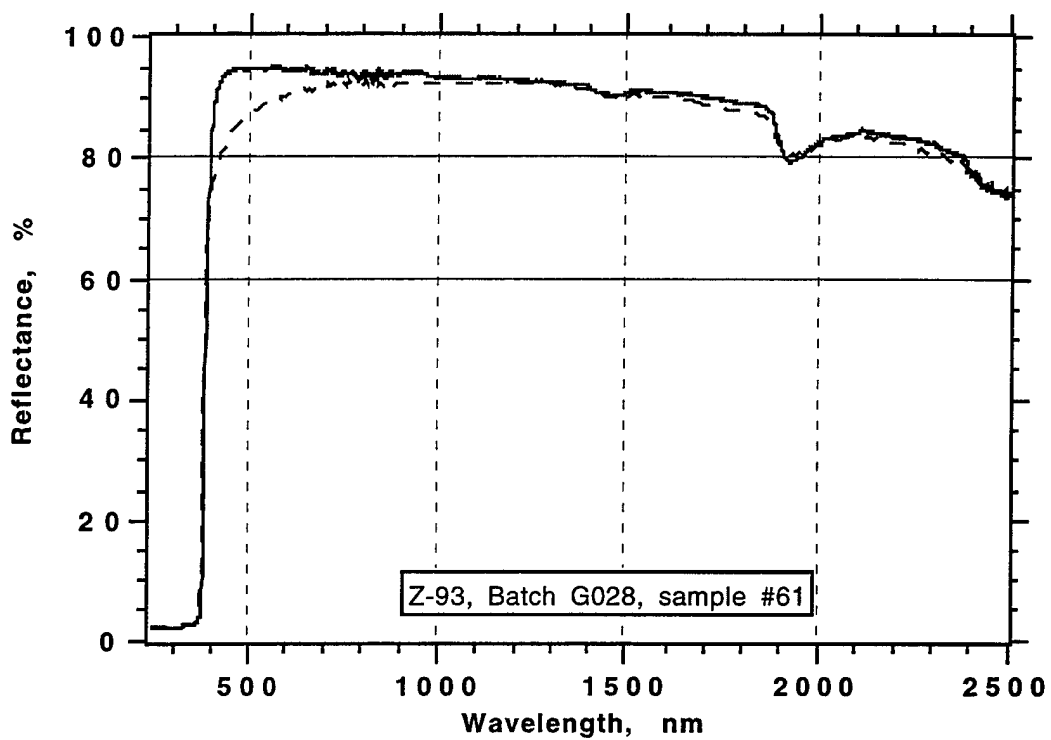
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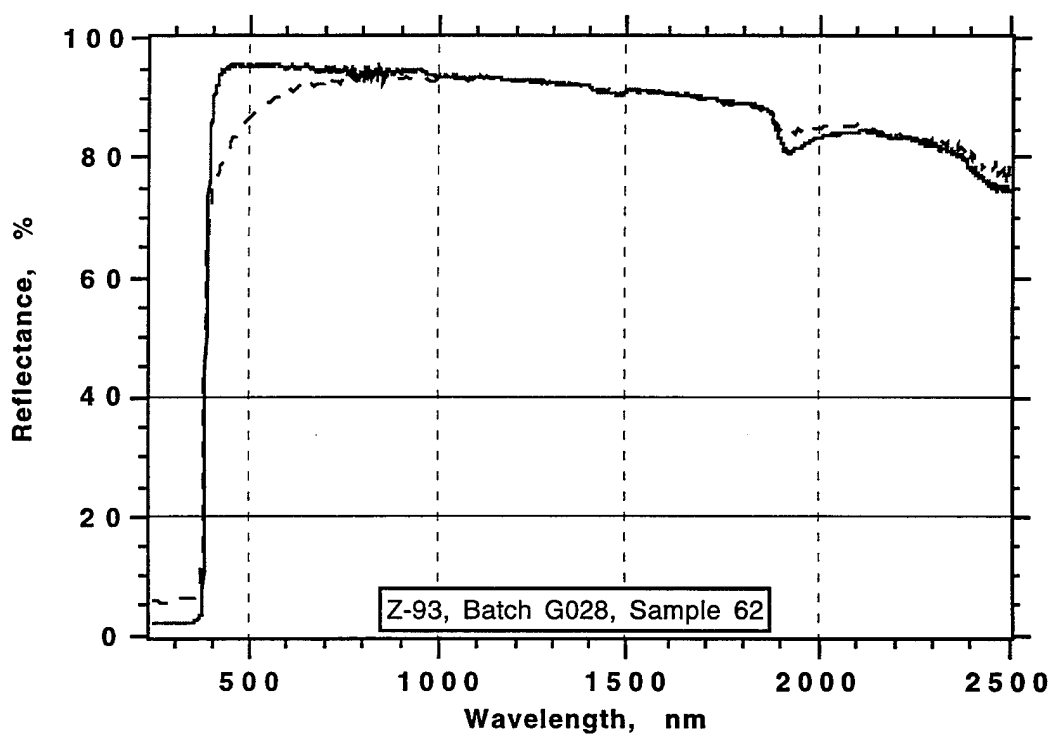
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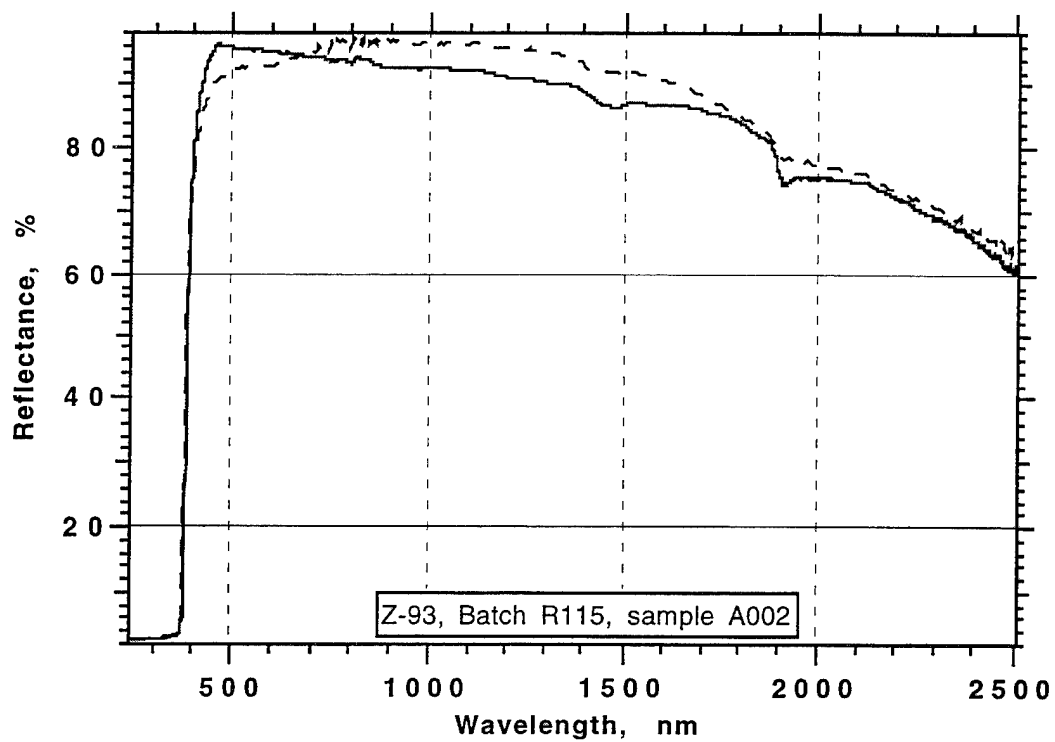
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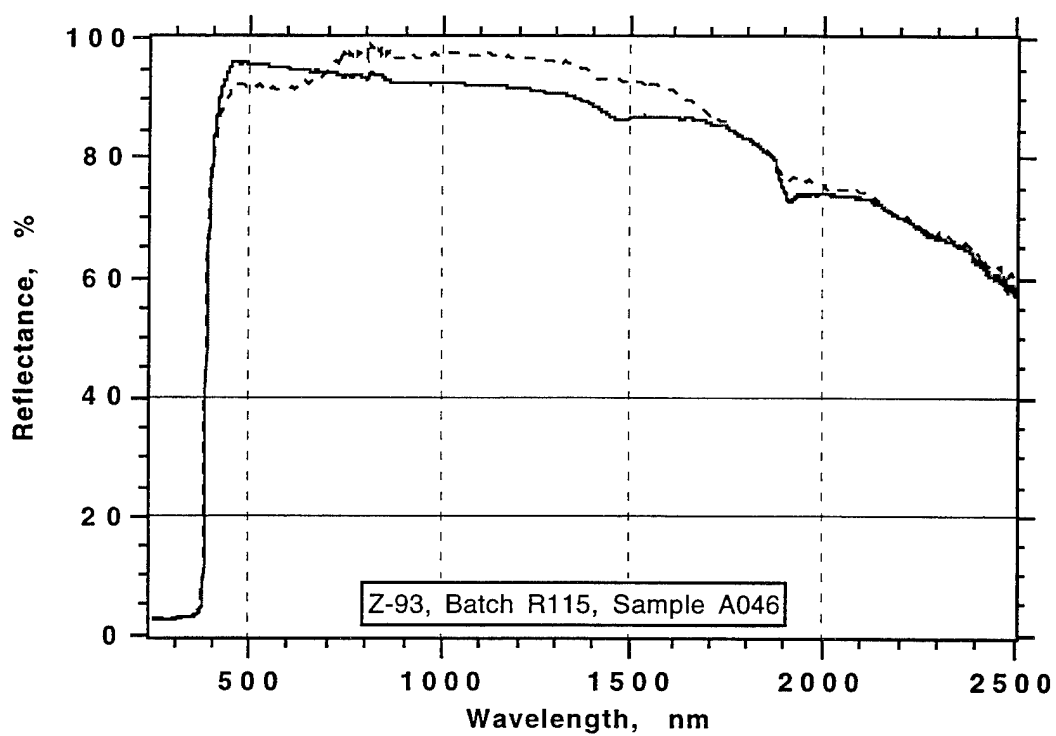
Graph 50.
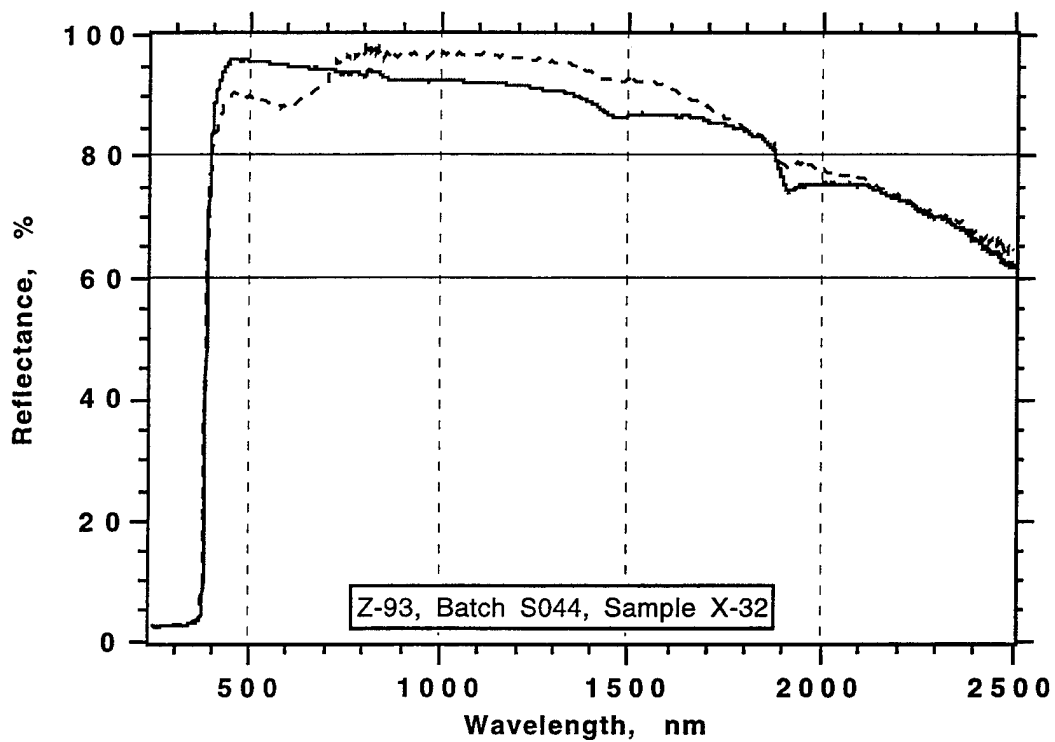
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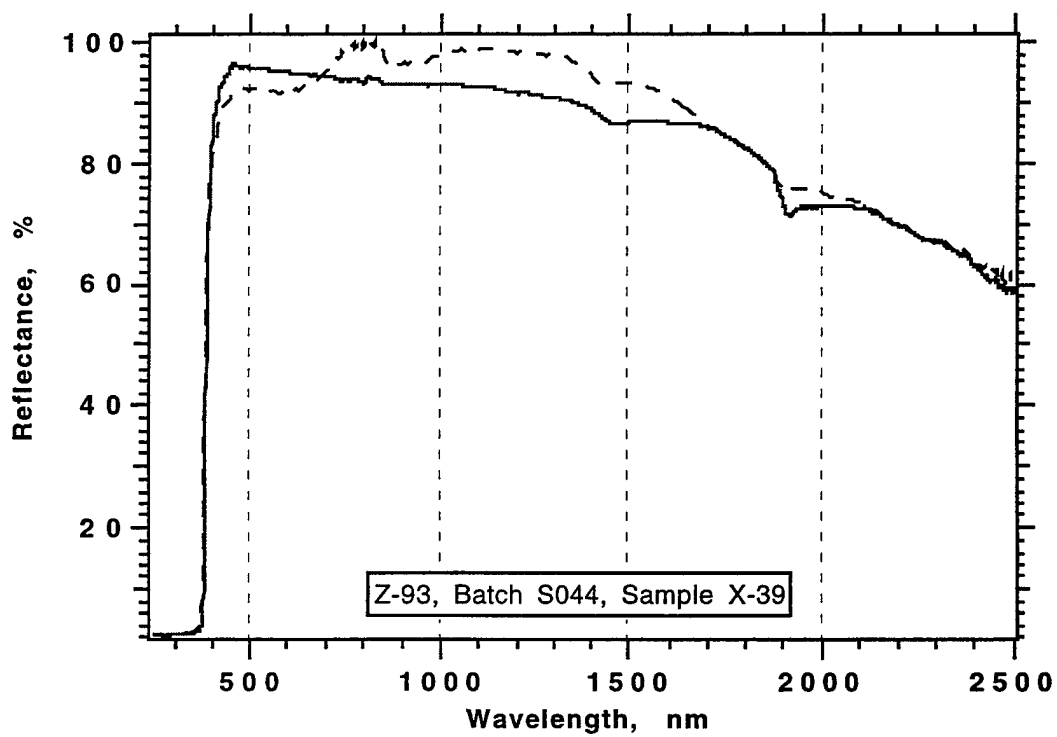
Graph 52.

Graph 53.

Graph 54.

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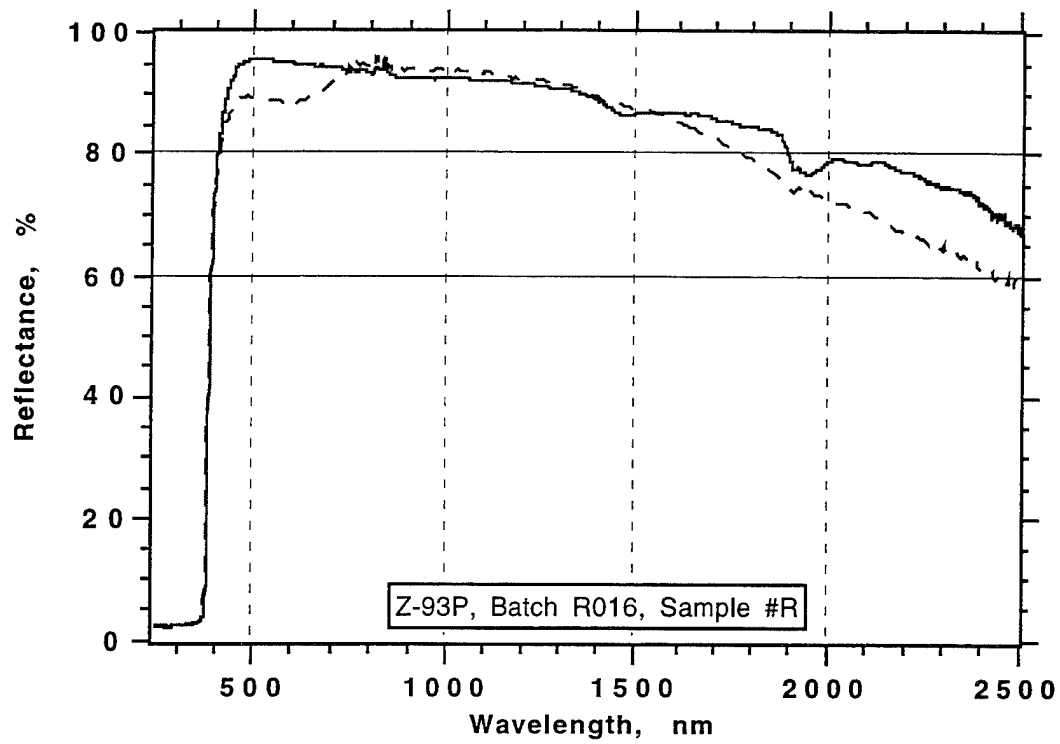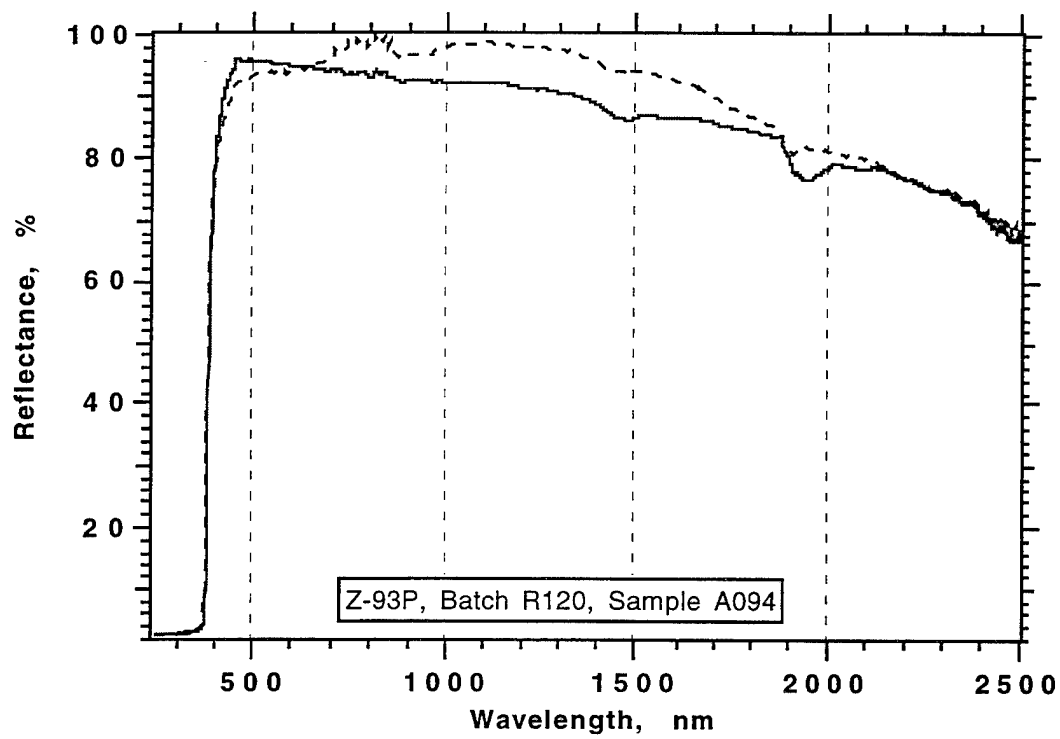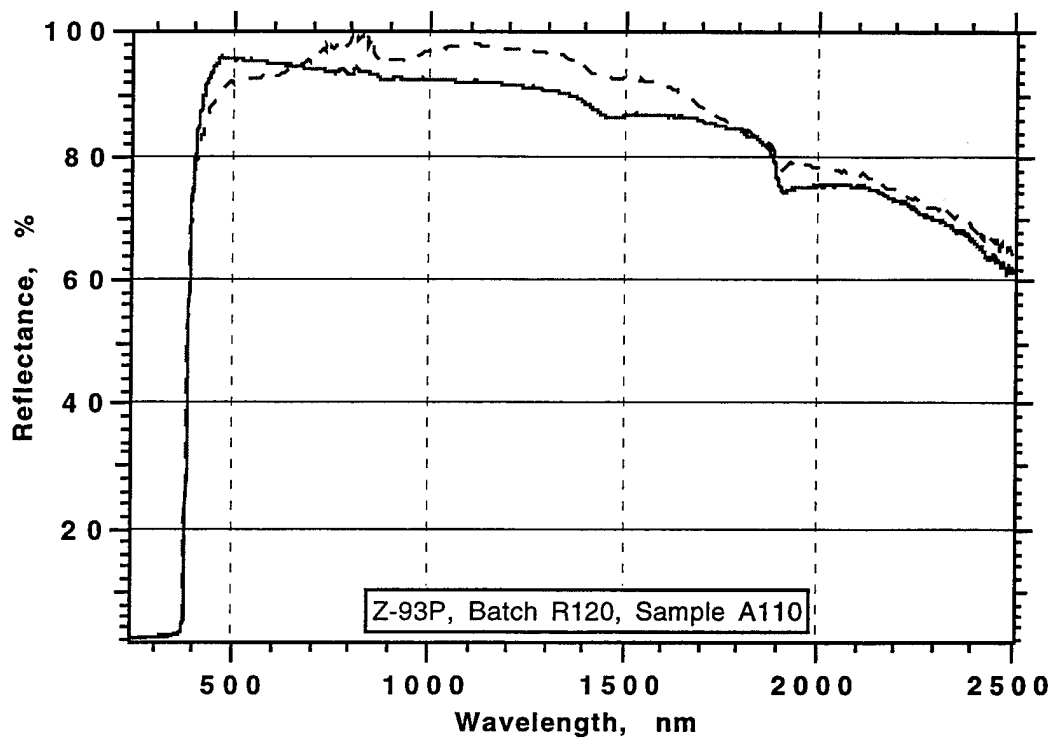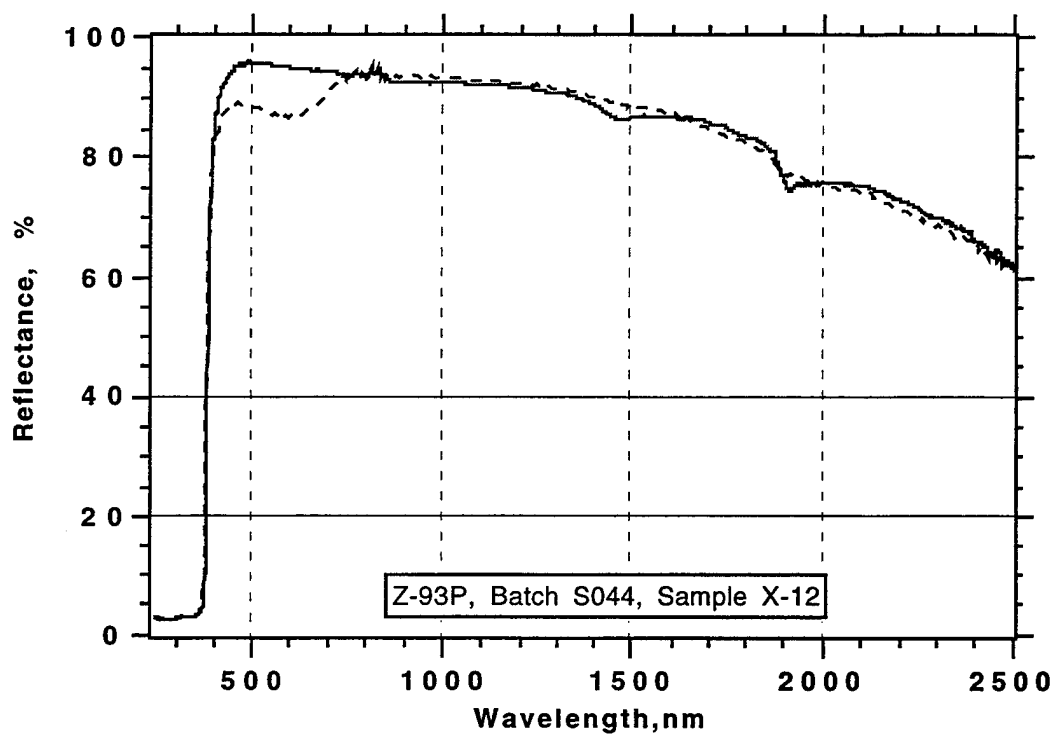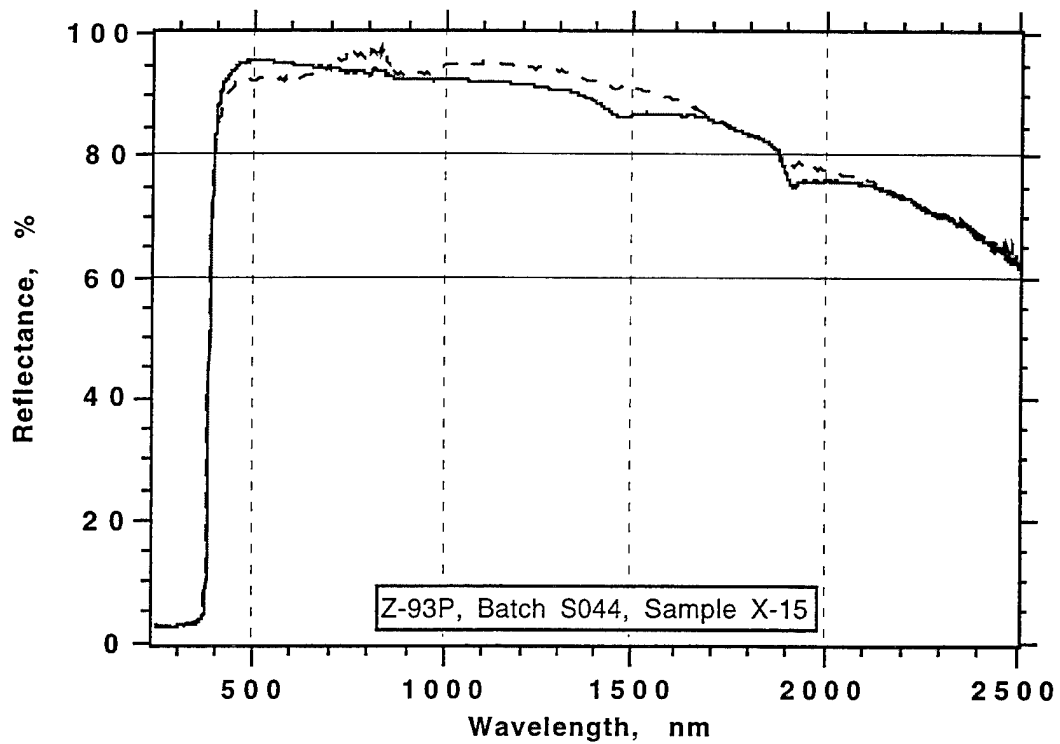
Graph 55.

Graph 56.

Graph 57.

Graph 58.

Graph 59.

Graph 60.

Graph 61.

Graph 62.

Graph 63.

Graph 64.

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S13GLO-1, Batch T114, Sample CH-1

Graph 65.

S13GLO-1, Batch T114, sample CH-2
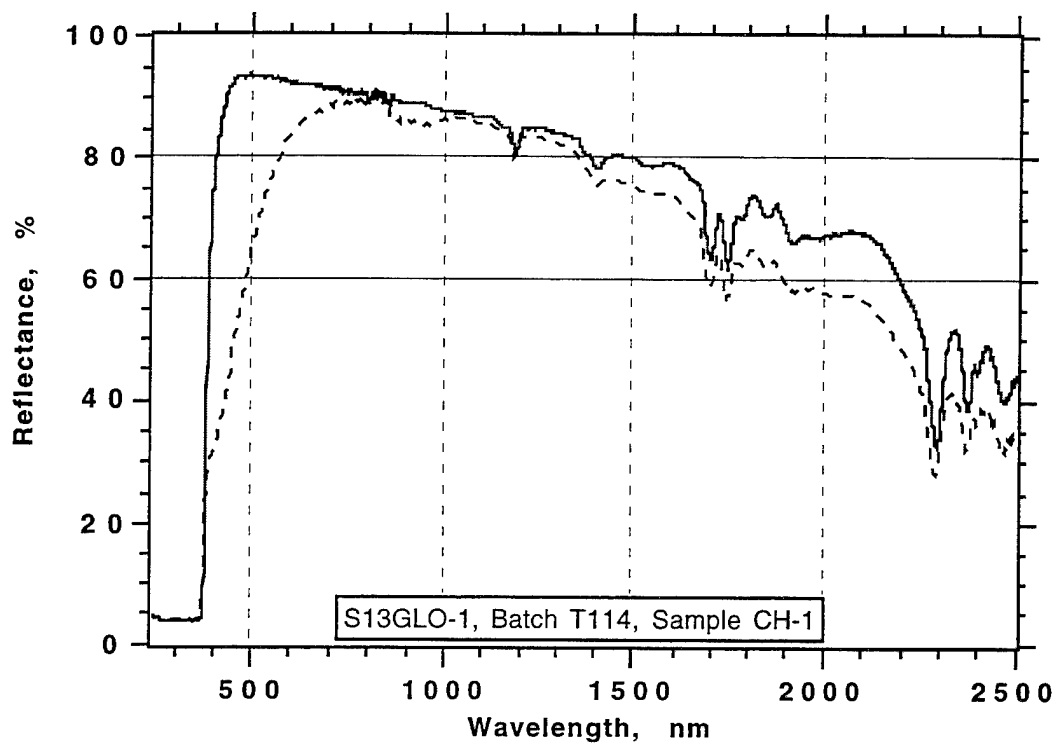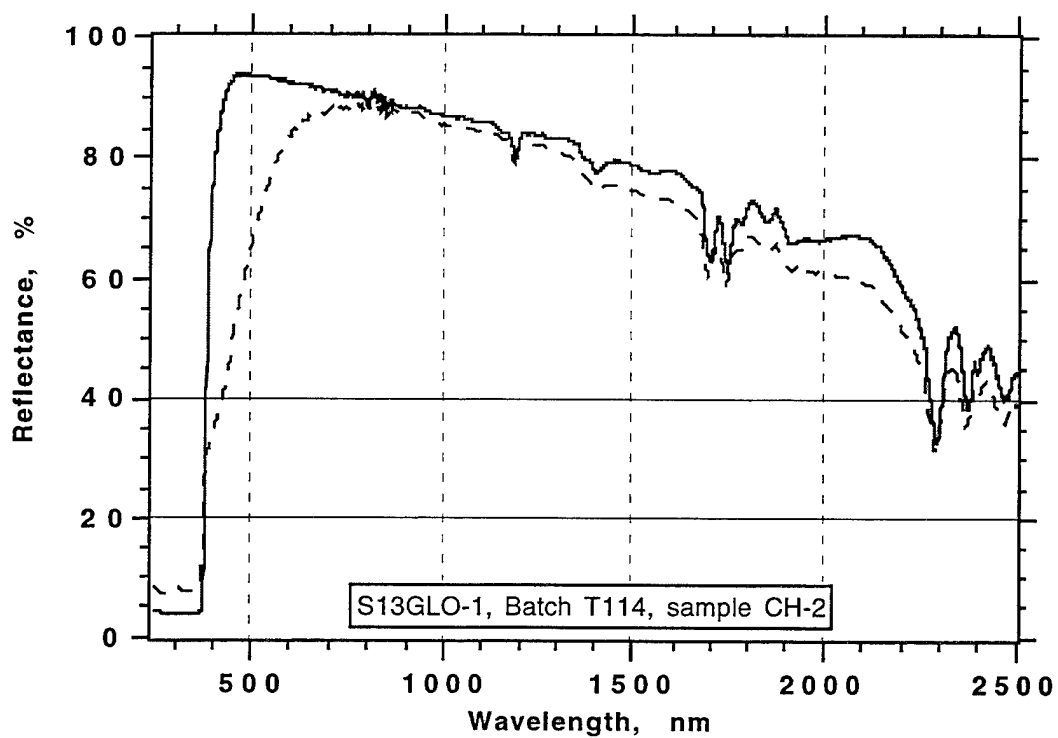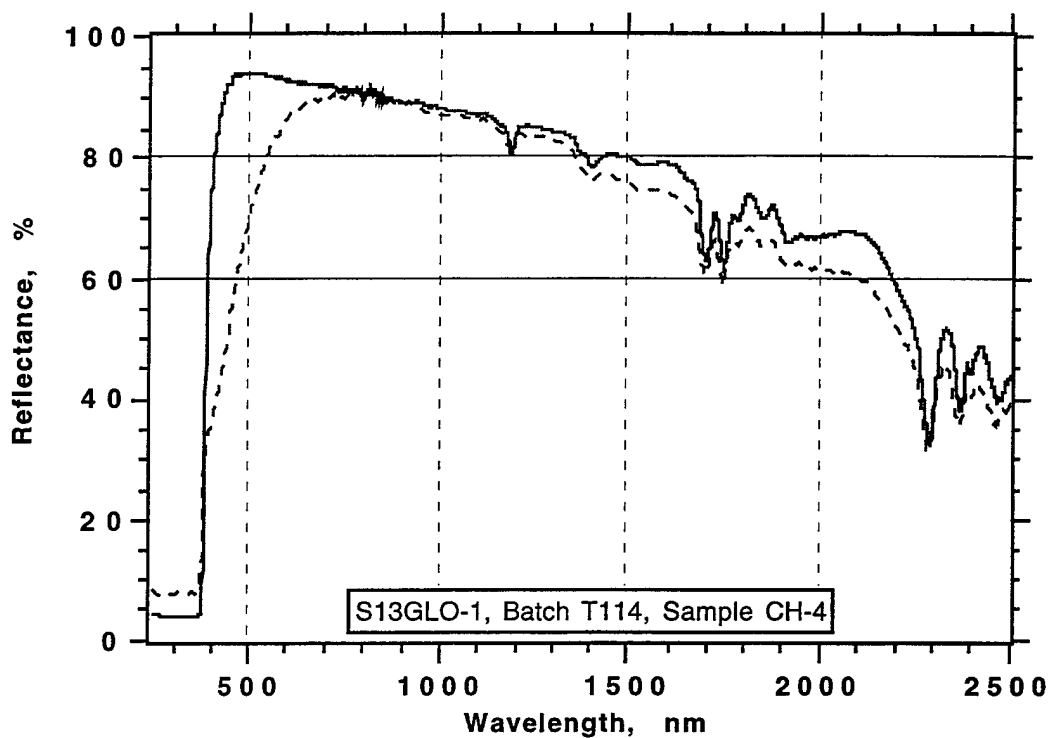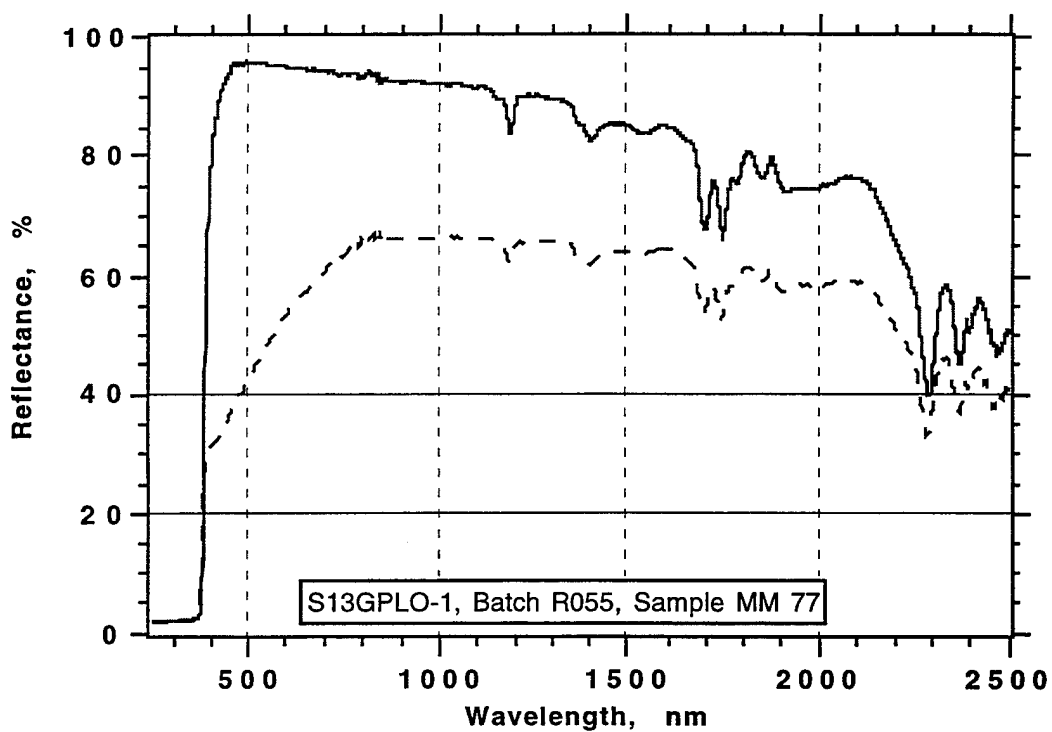
Graph 66.

Graph 67.

Graph 68.

Graph 69.

Graph 70.

Graph 71.

Graph 72.

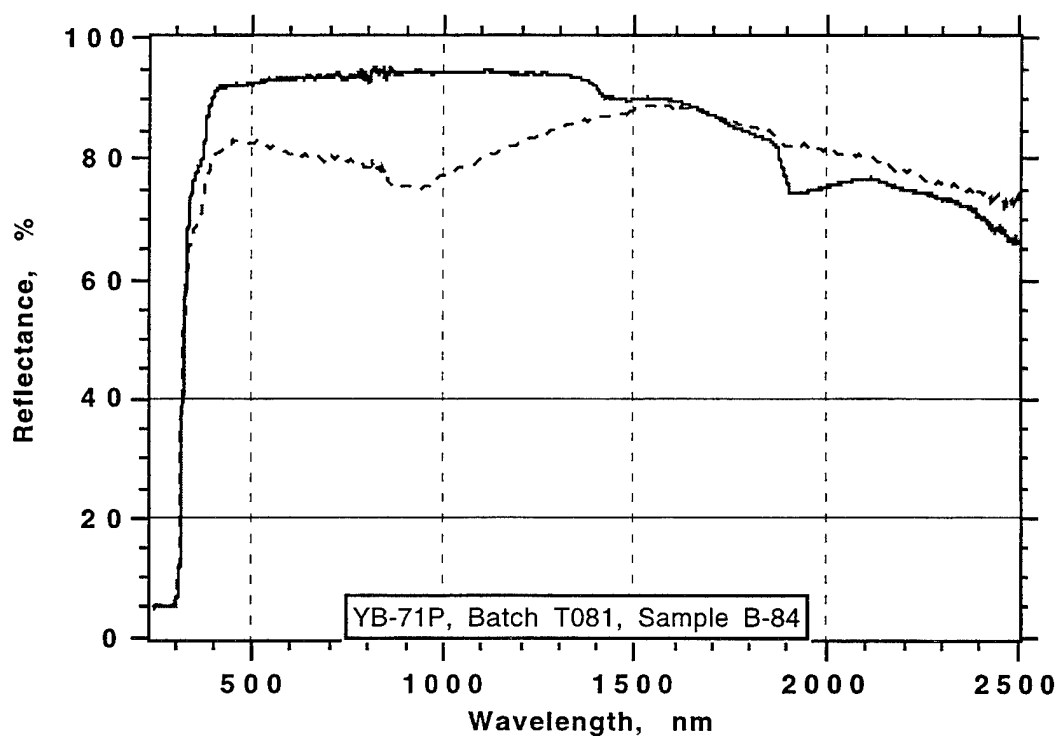Graph 73.
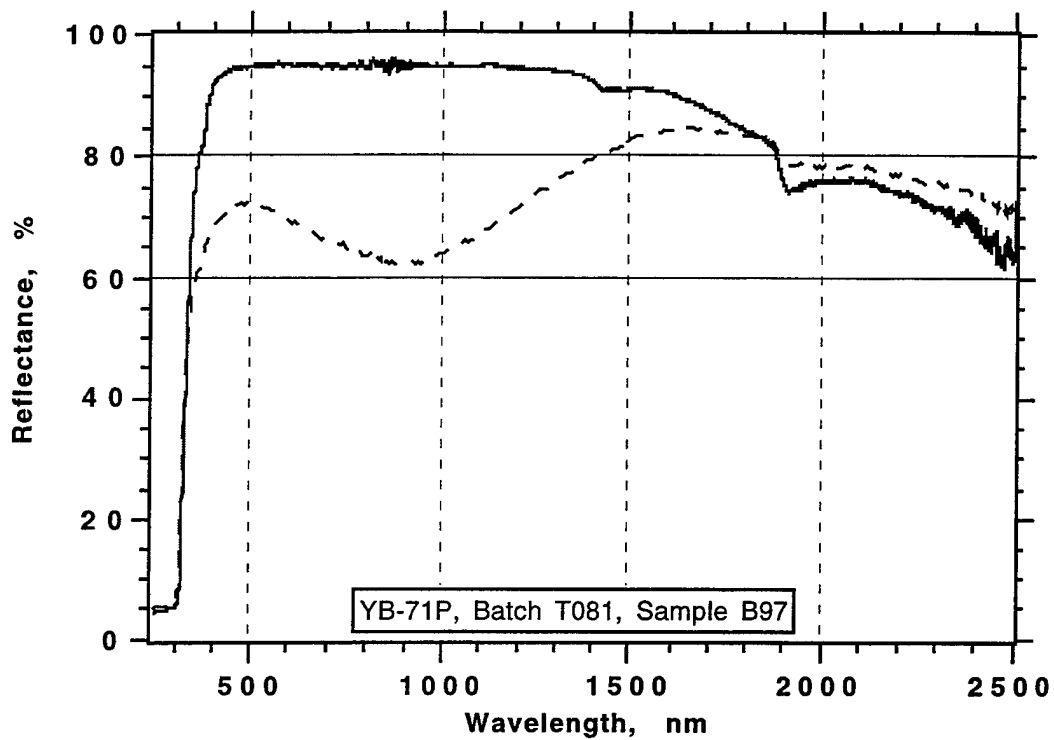

Graph 74.
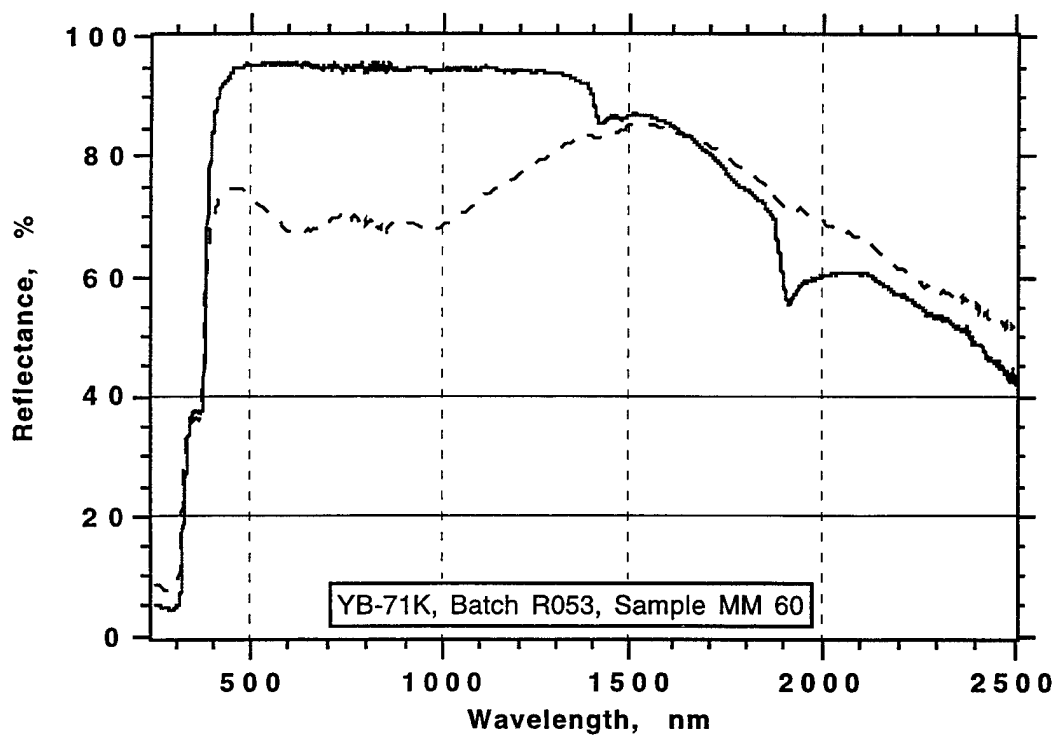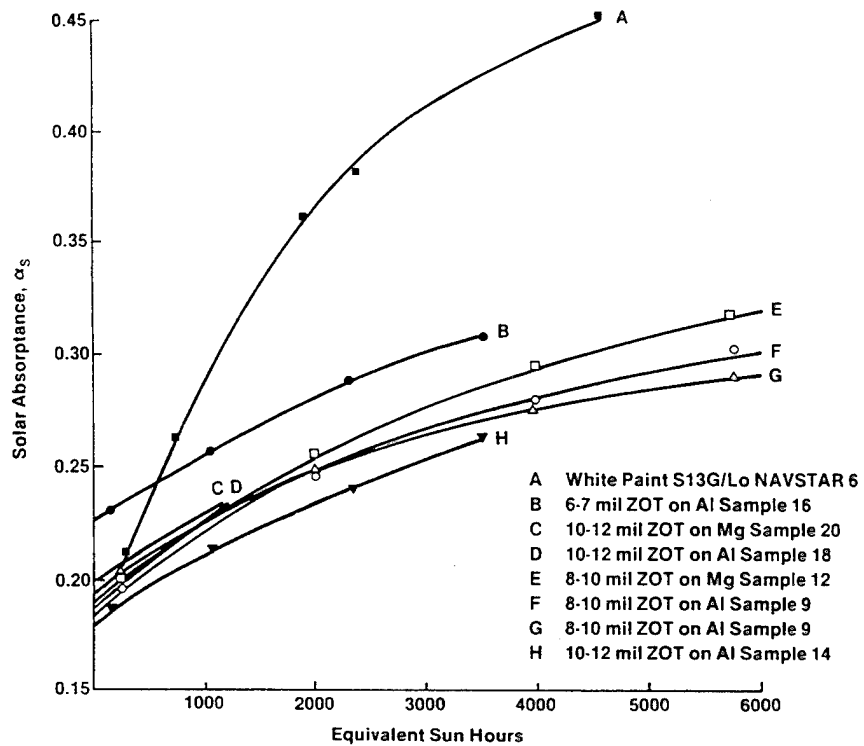
Graph 75.
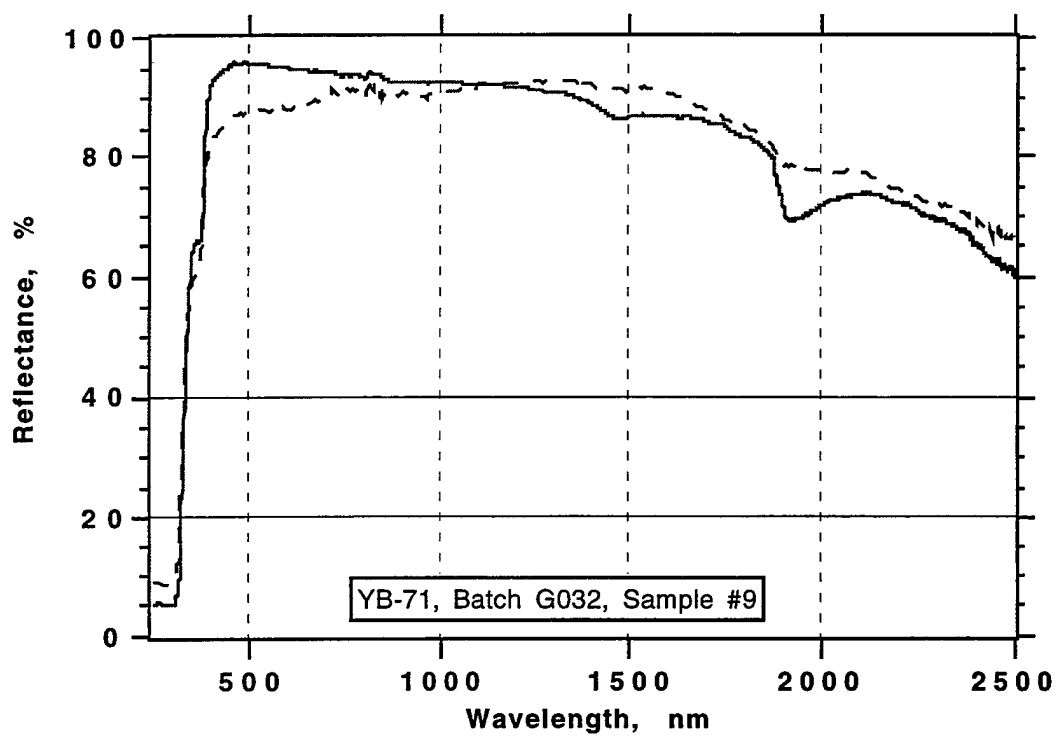
Graph 76.
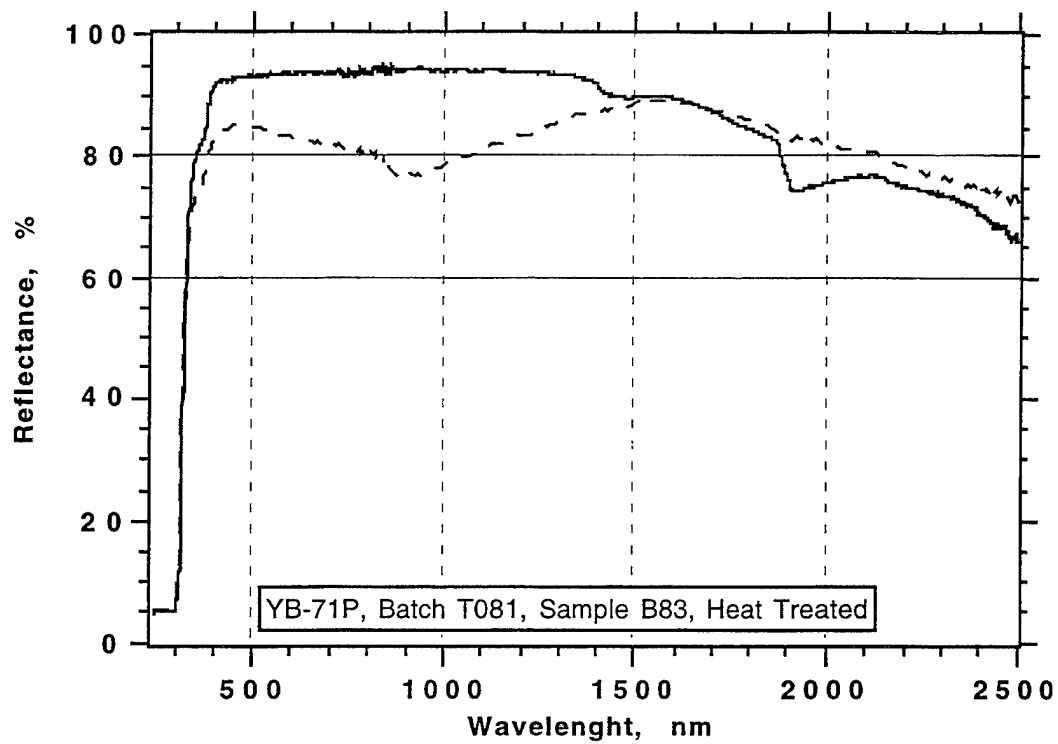
Graph 77.

Graph 78.

Graph 79.

Graph 80.

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Graph 81.

TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, Micro-Electro-Mechanical Systems (MEMS), and data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.